IMPROVED AND ENHANCED OIL RECOVERY IN ILLINOIS BY RESERVOIR CHARACTERIZATION

STANDARD OPERATING AND QA/QC PROCEDURES

Oil and Gas Section
Illinois State Geological Survey

OFS 1993-13

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ACKNOWLEDGEMENT

We acknowledge the support and contributions of Eileen M. Coleman who assembled several documents from different authors, consulted with authors regarding text and figures, and created eighteen detailed Freelance graphics for this manual.

This manual is intended to document experimental and other laboratory procedures used in the Illinois State Geological Survey's research project entitled: "Improved and Enhanced Oil Recovery in Illinois Through Reservoir Characterization" during the period June 28, 1989 through June 27, 1993. QA/QC documentation is included.

D. F. Oltz
Principal Investigator

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HAZARDOUS WASTE DISPOSAL

Dennis J. Haggerty

Whenever solvents, residues, or any contaminated waste is ready for disposal, the University of Illinois Hazardous Waste Department is notified by dialing 333-9278 and explaining what the waste is, the quantity, and whether or not the container should be returned. Within 48 hours a representative will haul the waste out. We have used this system for the disposal of toluene, acetone, and crude oil waste.

To dispose of solvents, residues or any contaminated waste, dial the University of Illinois 333-9278 and explain what the waste material is, the quantity and whether or not the container should be returned. The waste would normally be hauled out within 48 hours.

HELIUM POROSIMETER

Dennis J. Haggerty

Scope and Use of the Method

The Helium porosimeter is used to non-destructively determine the effective porosity of core samples with diameters up to 2.0" and as long as 3.469". The porosimeter is Temco's Model M-0100 equipped with two reference chambers that allow 10 different expansion methods. The accuracy of the method is primarily limited by the calibration of the digital pressure gauge and reference volumes within the plumbing system. The method has been tested for a calibrated test plug and sandstone core samples. This is a rapid method for measuring the grain volume of core samples as compared to a method of measuring the pore volume by saturating core samples with water or brine. The method is used for core analyses, core-log correlation and as a check on previously measured data.

General Principles

Initially, an unknown volume of Helium within a sample cup containing a core sample is expanded into reference chamber(s) of known volume at isothermal condition, or vice versa, to measure the grain volume of the sample by making use of the combined Boyle's law and Charles' law. This method includes expansions from the sample cup (SC) to the reference chamber(RC) 1, SC to RC 2, SC to RC 1 + RC 2, SC + RC 1 to RC 2, SC + RC 2 to RC 1, RC 1 to SC, RC 2 to SC, RC 1 to SC + RC 2, RC 2 to SC + RC 1, and RC 1 + RC 2 to SC, all with the toggle valve open or closed in the system from which expansion is to be made. Knowing the bulk volume of the sample, the grain volume is subtracted from the bulk volume to calculate the pore volume. The effective porosity is then calculated as the ratio of pore volume to bulk volume.

The method requires the calibration of reference volumes in the system prior to the grain volume determination. To this end, four or five expansion methods may be employed, using core disks instead of core samples in the sample cup. The reference volumes (fig. 1) consist of the volumes of a line from SC to its valve (V1), common lines (V2), RC 1 including the line to its valve (V3), RC 2 including the line to its valve (V4) and toggle valve when opened (V5). This method includes expansion from SC to RC 1 + RC 2, RC 1 to SC + RC 2, RC 2 to SC + RC 1, RC 1 + RC 2 to SC, SC to RC 1 + RC 2. A set of equations generated from the respective expansions may be solved simultaneously for the desired number of unknowns. The calculations for the effective porosity and reference volumes are performed in a Fortran 77 program, POROS.EXE, using a PC in an interactive mode.

It is recommended that V2 be included in the system from which expansion is to be made, since the instrument can not accurately read sample cup and chamber pressures with V2 excluded. In the event that V5 is to be determined it is essential that accurate

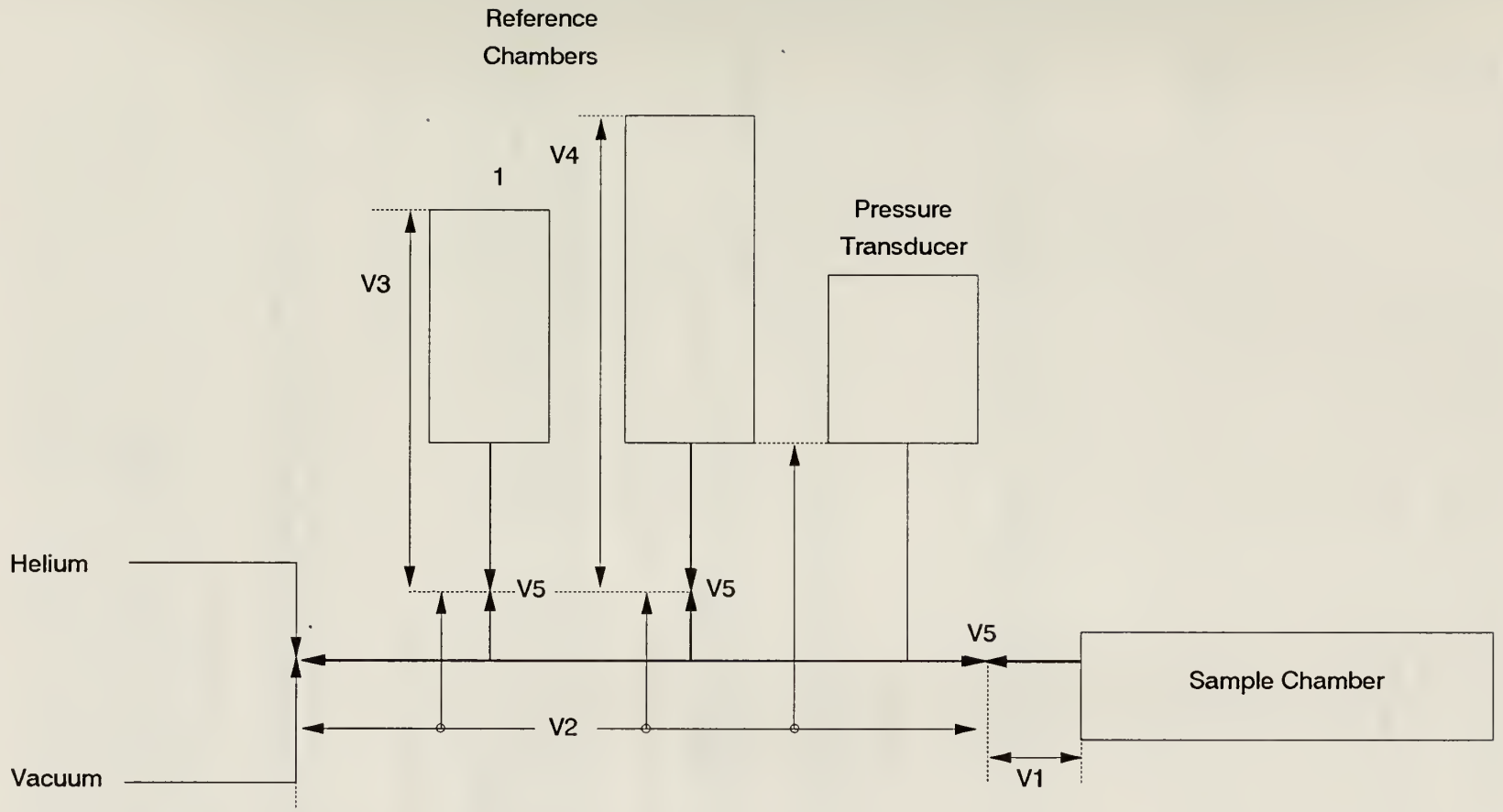


Figure 1. Helium Porosimeter Chambers and Valving

pressure data be recorded to 3 decimal points. The instrument goes out of calibration suddenly or slowly if foreign objects (such as condensed water, water or oil slugs, vapor or dirt) enter the system. As a consequence, the user should calibrate the reference volumes before and after taking each set of measurements. The digital pressure gauge may be calibrated by attaching a dead weight tester to the transducer and applying pressures up to 100 psia.

Equipment and Apparatus

Temco's M-0100 Helium porosimeter is equipped with a sample cup, two reference chambers (fig. 1), a digital absolute pressure gauge, and a helium tank equipped with a pressure regulator.

Procedure

Expansion from sample cup to reference chamber 1 + reference chamber 2 (note 1).

Single Expansion

1. Close all valves on the instrument.
2. Turn on the instrument and allow 20-30 minutes to warm up.
3. Open the helium tank valve and set regulator pressure up to 85 psig such that the maximum pressure in the system remains under 100 psia.
4. Replace enough volumetric disks with the core sample.
5. Open all three toggle valves for the sample cup and both reference chambers.
6. Pull a vacuum from the system to zero psia. Record the residual pressure, Pv within the vacuum system, if any.
7. Close the two reference chamber valves.
8. Open the main valve.
9. Let the pressure stabilize for 10 seconds and then close the main valve.
10. Record the stabilized initial pressure, Pi.
11. Open reference chamber 1 valve for single expansion.
12. Record the stabilized final expansion pressure, Pf (note 2).

Double Expansion

13. Open reference chamber 2 valve for double expansion.
14. Take the stabilized P_f reading (note 3).

Note 1. Measurements by making use of the other 8 expansion methods can be done in a similar manner to the above single and double expansions. In the expansions, V2 is included in the system from which expansion is to be made (here, the toggle valve of the system (i.e., sample cup valve) remains opened). If V2 is not to be included, pressurize the sample cup, and then close the sample valve to pull a vacuum on the other parts of the system.

Note 2. Continue to step 12 for double expansion.

Note 3. If more measurements are desired on the same core sample, repeat steps 5 through 14. For measurement on a different core sample, repeat steps 4 through 14. Upon final measurement, close the helium tank valve, remove the core from the sample cup with caution to reinsert the disks. Last, turn off the instrument.

Calculations

Equating Boyle's law and Charles' law for isothermal conditions yields:

$$Pi \cdot Vi = P_f \cdot V_f \quad (1)$$

For successive expansion in the system, equation 1 may be written as:

$$Pi \cdot \Sigma Vi + Pv \cdot \Sigma Vv = Pf \cdot \Sigma Vf \quad (2)$$

where P is the absolute pressure and V is the volume with subscripts i and f, initial and final, respectively. Pv is the residual pressure within the vacuum system and ΣVv is the chamber volume(s) into which expansion is made. The numerical value of ΣVv depends on how the expansion is made.

(1) Reference Volumes

With respect to the four or five expansion methods mentioned above, four simultaneous equations 3, 4, 5, and 6 or five simultaneous equations 3, 4, 5, 6, and 7 may be generated as follows:

$$Pi\,(V1+V2+V5+Vdr) + Pv \cdot \Sigma Vv = Pf\,(V1+V2+V3+V4+3V5+Vdr) \quad (3)$$
$$Pi\,(V2+V3+V5) + Pv \cdot \Sigma Vv = Pf\,(V1+V2+V3+V4+3V5+Vdr) \quad (4)$$
$$Pi\,(V2+V4+V5) + Pv \cdot \Sigma Vv = Pf\,(V1+V2+V3+V4+3V5+Vdr) \quad (5)$$
$$Pi\,(V2+V3+V4+2V5) + Pv \cdot \Sigma Vv = Pf\,(V1+V2+V3+V4+3V5+Vdr) \quad (6)$$
$$Pi\,(V1+V2+V3+V5+Vdr) + Pv \cdot \Sigma Vv = Pf\,(V1+V2+V3+V4+3V5+Vdr) \quad (7)$$

where Vdr is the volume of the removed disk. The Vdr numerical value should differ with Eqs. (see Table 1).

Eqs. (3), (4), (5), (6), and (7) may be arranged as

$$a(I) \cdot V1+b(I) \cdot V2 + c(I) \cdot V3+d(I) \cdot V4+e(I) \cdot V5 = f(I) \quad (8)$$

In matrix form,

$$A(I,J) \cdot B(I) = f(I) \quad (9)$$

where A(I,J) is the coefficient matrix consisting of a(I), b(I), c(I), d(I), and e(I); B(I) is the solution vector containing V1, V2, V3, V4 and V5 as five unknowns, or V1 +V5, V2, V3+V5 and V4+V5 as four unknowns; and f(I) is the summation of known values including Vdr, Vv and the products of pressure and V5.

Table 1. Disk (Spacer Plug) Dimension

No.	Diameter		Height		Volume	
	(cm)	(in)	(cm)	(in)	(cc)	(ci)
1	2.667	1.05	0.3175	0.125	1.774	0.108
2	2.667	1.05	0.9525	0.375	5.321	0.325
3	2.667	1.05	1.2700	0.500	7.095	0.433
4	2.667	1.05	2.2225	0.875	12.416	0.758
5	2.667	1.05	2.7781	1.094	15.519	0.947

Effective Porosity

Based on equation 2 and the above mentioned expansion methods, ten equations may be obtained:

SC to RC1:

$$Pi(V1+V2+V5+x)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+2V5+x) \quad (10)$$

SC to RC2:

$$Pi(V1+V2+V5+x)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V4+2V5+x) \quad (11)$$

SC to RC1+RC2:

$$Pi(V2+V4+V5+x)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (12)$$

SC+RC1 to RC2:

$$Pi(V1+V2+V3+2V5+x)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (13)$$

SC+RC2 to RC1:

$$Pi(V1+V2+V4+2V5+x)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (14)$$

RC1 to SC:

$$Pi(V2+V3+V5)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+2V5+x) \quad (15)$$

RC2 to SC:

$$Pi(V2+V4+V5)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V4+2V5+x) \quad (16)$$

RC1 to SC+RC2:

$$Pi(V3+V5)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (17)$$

RC2 to SC+RC1:

$$Pi(V2+V4+V5)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (18)$$

RC1 + RC2 to SC:

$$Pi(V2+V3+V4+2V5)+\Sigma(Pv \cdot Vv) = Pf(V1+V2+V3+V4+3V5+x) \quad (19)$$

with

$$x=Vdr-Vg \quad (20)$$

where

Vg is the grain volume of the core sample.

Rearranging the ten equations yields:

$$x = (Pf \cdot \Sigma Vf - Pi \cdot \Sigma Vi - Pv \cdot \Sigma Vv) / (Pi - Pf) \quad (21)$$

or

$$x = (Pi / Pf) \cdot \Sigma Vi + (Pv / Pf) \cdot \Sigma Vv - \Sigma Vf \quad (22)$$

Eqs. (10), (11), (12), (13), and (14) fall into the form of equation (21), and Eqs. (15), (16), (17), (18), and (19) into the form of equation (22). After calculating x from equation (21) or equation (22), the grain volume, Vg can be obtained from equation 20.

The above calculations for reference volumes and the effective porosity by 10 different expansion methods are performed in a Fortran 77 computer program, POROS. The program can be run in an interactive mode on PC. Step by step instructions appear on the screen for data input and running options. The program listing, user's manual and example computation are included in this Standard Operating Procedure.

Precision and Accuracy

The accuracy of the method depends on the digital pressure gauge used. The model D-2000 equipped in the instrument provides specified accuracy of + or - 0.1 psia. the overall precision and accuracy of this method varies with the expansion pressure range and atmospheric pressure changes during the test. Factors influencing the precision and accuracy of the instrument include the temperature drop between the helium source tank and the system within the instrument (Joule-Thompson effect), magnitude of volume change caused by the compression of the o-ring in the sample cup for differing pressures, air compressibility in the system, and any residual pressures within the vacuum system.

Recommended Procedure for Quick Results

1. Allow a 20 minute warm-up for the gauge and vacuum pump.

2. Adjust cup holder so that the o-ring seals tightly against the plate by turning adjustment bolt.

3. Pressure entire system up to 70 psia and observe. Eliminate any leaks for at least 5 minutes.

4. Evacuate entire system until pressure is 0.00 psia or very close.

5. Run calibration routine once (without recording data); look for leaks.

6. Run calibration routine and run the program to make sure results are valid.

7. Without further adjustments, run expansion procedures 11, 12 and 17 (the most rapid and reliable); record the data, then continue with the next sample. Shut the system down only after all the samples are run (continuity is the key).

8. Repeat the above steps if more than 4 hours elapse, because changes in barometric pressure can affect the results.

POROS Program Listing

```
C     FORTRAN PROGRAM - POROS
C     AUTHOR : HWI W. BANG
C     DATE : AUGUST 1989
C     O&G, ISGS INCLUDE 'PI.INC' DIMENSION VDPIF(N,4) CHARACTER*8
      RUNCONT,DATANAME,CORENAME,RNEWDATA,RNEWCORE CHARACTER*8
      DN(MNDS),ANO,RD,RCVB,V2INC COMMON/AAA/ VDRC,VDRI,VDRF,PI,PF
      COMMON/BBB/ POR(MNDS) COMMON/CCC/ A(N,NPM) DATA ANO/1HN/,RD/1HR/
      WRITE (6,370) READ (5,460) PART12 IF (IFIX(PART12) .EQ. 2) GO TO 100
```

```
C     *** PART 1 ***
      WRITE (6,400)
   10 WRITE (6,250)
      READ (5,360) DATANAME
      DO 30 I=l,N
      DO 20 J=MPl,NPM
   20 A(I,J)=O.O
   30 A(I,M+I)=1.0
      IF (N .EQ. 5) GO TO 31
      WRITE (6,340)
      READ (5,460) V5
   31 DO 70 I=1,N
      WRITE (6,610) I
      WRITE (6,620)
      READ (5,460) PV
      CALL RDWRT (3)
      GO TO (35,40,45,50,55) I
   35 CALL COEFF (1.,1.,0.,0.,1.,VDRI,1.,1.,1.,1.,3.,VDRF,A(I,1),
     * A(I,2),A(I,3),A(I,4),A(I,5),RHS)
      A(I,3) = A(I,3) + PV
      A(I,4) = A(I,4) + PV
      GO TO 60
   40 CALL COEFF (O.,l.,l.,O.,l.,VDRI,1.,1.,1.,1.,3.,VDRF,A(I,l),
     * A(I,2),A(I,3),A(I,4),A(I,5),RHS)
      A(I,l) = A(I,l) + PV
      A(I,4) = A(T,4) + PV
      GO TO 60
   45 CALL COEFF (0.,1.,0.,1.,1.,VDRI,1.,1.,1.,1.,3.,VDRF,A(I,l),
     * A(I,2),A(I,3),A(I,4),A(I,5),RHS)
      A(I,l) = A(I,l) + PV
      A(I,3) = A(I,3) + PV
      GO TO 60
   50 CALL COEFF (0.,1.,1.,1.,2.,VDRI,1.,1.,1.,1.,3.,VDRF,A(I,l),
     * A(I,2),A(I,3),A(I,4),A(I,5),RHS)
      A(I,1) = A(I,1) + PV
      GO TO 60
   55 CALL COEFF (1.,1.,1.,0.,2.,VDRI,1.,1.,1.,1.,3.,VDRF,A(I,l),
     * A(I,2),A(I,3),A(I,4),A(I,5),RHS)
      A(I,4) = A(I,4) + PV
   60 IF (N .EQ. 4) A(I,M) = RHS - A(I,5) * V5
      IF (N .EQ. 5) A(I,M) -- RHS
      VDPIF(I,l) = VDRI
      VDPIF(I,2) = PI
      VDPIF(I,3) = VDRF
      VDPIF(I,4) = PF
   70 CONTINUE
      WRITE (6,590)
```

```
      DO 80 I=l,N
   80 WRITE (6,600) I,(VDPIF(I,J),J=1,4)
      WRITE (6,260) N,NPM
      DO 85 I=l,N
   85 WRITE (6,270) (A(I,J),J=1,NPM) CALL GAUSSJ
      WRITE (6,260) N,NPM
      DO 90 I=l,N
   90 WRITE (6,270) (A(I,J),J_1,NPM)
      CALL HOUSE (2)
      WRITE (6,530) DATANAME
      WRITE (6,480)
      IF (N .EQ. 4) A(M,M) = V5
      WRITE (6,290) (I,A(I,M),İ=l,M)
      WRITE (6,295)
      CALL HOUSE (1)
      Vl = A(l,M)
      V2 = A(2,M)
      V3 = A(3,M)
      V4 = A(4,M)
      IF (N .EQ. 5) V5 = A(N,M)
      WRITE (6,510)
      READ (5,360) RNEWDATA
      IF (RNEWDATA .NE. ANO) GO TO 10
      WRITE (6,350)
      READ (5,360) RUNCONT
      IF (RUNCONT .EQ. ANO) CALL EXIT

C   *** PART 2 ***
  100 WRITE (6,470)
      IF (IFIX(PART12) .EQ. 1) GO TO 105
      WRITE (6,250)
      READ (6,360) DATANAME
      WRITE (6,300)
      READ (5,460) Vl
      WRITE (6,310)
      READ (5,460) V2
      WRITE (6,320)
      READ (5,460) V3
      WRITE (6,330)
      READ (5,460) V4
      WRITE (6,340)
      READ (5,460) V5
  105 WRITE (6,280)
      READ (5,360) V2INC
      V2I = V2
      V5I = V5
      IF (V2INC .EQ. ANO) V2I = 0.
```

```
      IF (V2INC .EQ. ANO) V5I = 0.
      IF (IFIX(PART12) .EQ. 1) GO TO 110
      A(1,5) = Vl
      A(2,5) = V2
      A(3,5) = V3
      A(4,5) = V4
      A(5,5) = V5
      CALL HOUSE (2)
      WRITE (6,530) DATANAME
      WRITE (6,480)
      WRITE (6,290) (I,A(I,5), I=1,5)
      WRITE (6,295)
      CALL HOUSE (1)
110   WRITE (6,520)
      READ (5,360) CORENAME
      WRITE (6,250)
      READ (5,360) DATANAME
      NDS = 1
      CALL RDWRT (1)
      WRITE (6,490)
      READ (5,360) RCVB
      IF (RCVB .EQ. RD) GO TO 120
      WRITE (6,380)
      READ (5,460) DC
      WRITE (6,390)
      READ (5,460) HC
      VB = 3.14159 * (0.5*DC)**2 * HC
      GO TO 125
120   WRITE (6,410)
      READ (5,460) VB
125   WRITE (6,620)
      READ (5,460) PV
      CALL RDWRT (2)
      WRITE (6,420)
      READ (5,460) EXPNSN
      GO TO (130,140,145,150,155,160,170,180,190,200) IFIX(EXPNSN)
130   VDRMG = VDRMG2 (V1,V2,V3,0.,2*V5,Vl,V2I,0.,0.,V5I,PI,PF,PV,V3,0)
      GO TO 210
140   VDRMG = VDRMG2 (Vl,V2,0.,V4,2*V5,Vl,V2I,0.,0.,V5I,PI,PF,PV,V4,0)
      GO TO 210
145   VDRMG = VDRMG2 (Vl,V2,V3,V4,3*V5,Vl,V2I,0.,0.,V5I,PI,PF,PV,V3,V4)
      GO TO 210
150   VDRMG = VDRMG2 (Vl,V2,V3,V4,3*V5,Vl,V2I,V3,0.,2*V5I,PI,PF,PV,V4,0)
      GO TO 210
155   VDRMG = VDRMG2 (V1,V2,V3,V4,3*V5,Vl,V2I,0.,V4,2*V5I,PI,PF,PV,V3,0)
      GO TO 210
160   VDRMG = VDRMG1 (0.,V2I,V3,0.,V5I,Vl,V2,V3,0.,2*V5,PI,PF,PV,V1,0)
```

```
      GO TO 210
170   VDRMG = VDRMG1 (0.,V2I,0.,V4,V5I,V1,V2,0.,V4,2*V5,PI,PF,PV,V1,0)
      GO TO 210
180   VDRMG = VDRMG1 (0.,V2I,V3,0.,V5I,Vl,V2,V3,V4,3*V5,PI,PF,PV,Vl,V4)
      GO TO 210
190   VDRMG = VDRMG1 (0.,V2I,0.,V4,V5I,Vl,V2,V3,V4,3*V5,PI,PF,PV,Vl,V3)
      GO TO 210
200   VDRMG = VDRMG1 (0.,V2I,V3,V4,2*V5I,Vl,V2,V3,V4,3*V5,PI,PF,PV,Vl,0)
210   VG = VDRC - VDRMG
      VP = VB - VG
      POR(NDS) = VP / VB
      CALL HOUSE (2)
      WRITE (6,540) CORENAME,DATANAME
      IF (RCVB .EQ. RD) GO TO 220
      WRITE (6,480)
      WRITE (6,430) DC,HC
220   WRITE (6,500) VB,VDRC,PV,PI,PF
      WRITE (6,480)
      WRITE (6,440) POR(NDS),VP,VG,IFIX(EXPNSN),V2INC
      CALL HOUSE (1)
      DN(NDS) = DATANAME
      WRITE (6,550)
      READ (5,360) RNEWDATA
      IF (RNEWDATA .EQ. ANO) GO TO 230
      WRITE (6,250)
      READ (5,360) DATANAME
      NDS = NDS + 1
      GO TO 125
230   CALL HOUSE (2)
      WRITE (6,580) CORENAME
      WRITE (6,480)
      DO 240 I=1,NDS
240   WRITE (6,560) DN(I),POR(I)
      CALL STDMV (NDS,PORMEAN,STDV,VAR)
      WRITE (6,570) PORMEAN,STDV,VAR
      CALL HOUSE (1)
      WRITE (6,450)
      READ (5,360) RNEWCORE
      IF (RNEWCORE .NE. ANO) GO TO 110
      STOP
250   FORMAT (1X,'ENTER DATA SET NAME :  ')
260   FORMAT (/5X,'A(1,1)...A(',Il,',',I2,')')
270   FORMAT (3X,11F7.2)
280   FORMAT (' V2 INCLUDED IN INITIAL VOLUME (TYPE IN Y OR N) ?  ')
290   FORMAT (5X,'*',2X,'  V',I1,' =',F8.3,' CC OR CI',40X,'*')
295   FORMAT (5X,'*',4X,'(WHEN V5 IS PRINTED AS ZERO ABOVE,',2X,'V1,',
     *  ' V3 AND V4',12X,'*'/5X,'*',5X,'INCLUDES THEIR TOGG',
```

```
 *   'LE VALVE VOLUMES)',24X,'*')
300  FORMAT (' VOLUME BETWEEN SAMPLE VALVE AND CUP - CC OR CI (Vl) = ')
310  FORMAT (' VOLUME BETWEEEN ALL VALVES - CC OR CI          (V2) = ')
320  FORMAT (' VOLUME OF REFERENCE CHAMBER 1 - CC OR CI       (V3) = ')
330  FORMAT (' VOLUME OF REFERENCE CHAMBER 2 - CC OR CI       (V4) = ')
340  FORMAT (' VOLUME OF TOGGLE VALVE WHEN OPENED - CC OR CI (V5) = ')
350  FORMAT (' CONTINUE TO RUN PART 2 (TYPE IN Y OR N) ?
360  FORMAT (A)
370  FORMAT (' RUN PART 1 OR PART 2 (TYPE IN 1 OR 2) ? ')
380  FORMAT (' CORE DIAMETER IN CM OP IN = ')
390  FORMAT (' HEIGHT OF CORE IN CM OR IN = ')
400  FORMAT (///1X,'***** PART 1 *****'//)
410  FORMAT (' BULK VOLUME OF CORE IN CC OR CI = ')
420  FORMAT (' EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR ',
 *   '10) ? ')
430  FORMAT (5X,'*','    DC = ',F8.3,' CM OR IN',5X,' HC = ',F8.3,
 *       ' CM OR IN',8X,'*')
440  FORMAT (5X,'*','    POROSITY = ',F6.3,' (WITH VP = ',F6.3,
 *   3X,'VG =',F6.3,' CC OR CI)',3X,'*'/5X,'*',22X,
 *   '(EXPANSION METHOD USED =',I2,' V2INC = ',A1,')',3X,
 *
     '*')
450  FORMAT (1X,'RUN FOR NEW CORE SAMPLE (TYPE IN Y OR N) ?
460  FORMAT (F20.0)
470  FORMAT (///1X,'***** PART 2 *****'//)
480  FORMAT (5X,'*',65X,'*')
490  FORMAT (' READ IN(R) OR COMPUTE(C) BULK ','VOLUME OF CORE (TYPE ',
 *   'IN R OR C) ? ')
500  FORMAT (5X,'*','    VB =',F8.3,' CC OR CI ',7X,' VDRC =',F8;3,
 *   ' CC OR CI ',7X,'*'/5X,'*',' PVAC =',F6.2,' PSIA ,4X,
 *   'PI =',F7.2,' PSIA',4X,'PF =',F7.2,' PSIA',4X,'*')
510  FORMAT (1X,'RERUN PART 1 FOR NEW DATA SET (TYPE IN Y OR N) ? ')
520  FORMAT (1X,'ENTER CORE SAMPLE NAME : ')
530  FORMAT (5X,'*',4X,'DATA SET NAME : ',A,37X,'*')
540  FORMAT (5X,'*',4X,'CORE SAMPLE NAME : ',A,' (DATA SET NAME : ',A,
 *   ')',7X,'*')
550  FORMAT (1X,'RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE
     IN',
 *   ' Y OR N) ? ')
560  FORMAT (5X,'*',19X,'POR (',A,') = ',F7.3,22X,'*')
570  FORMAT (5X,'*',38X,5(lH=),22X,'*'/5X,'*',19X,'POROSITY(MEAN) = ',
 *   F7.3,22X,'*'/5X,'*',15X,'STANDARD DEVIATION = ',F7.3,1X,
 *   '(VARIANCE = ',F5.3,')',3X,'*')
580  FORMAT (5X,'*',4X,'SUMMARY',lX,'(CORE SAMPLE NAME : ',A,')',24X,
 *   '*'/5X,'*',4X,7(1H+),54X,'*')
590  FORMAT (//13X,'I',8X,'VDRI',10X,'PI',10X,'VDRF',10X,'PF',/12X,
 *   '***',6X,6(1H*),3(7X,6('*')))
```

```
600  FORMAT (I14,4F13.3)
610  FORMAT (/' EXPANSION NO.',I2)
620  FORMAT (' RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = ')
     END

     SUBROUTINE COEFF (A1,B1,C1,D1,El,Fl,A2,B2,C2,D2,E2,F2,A,B,C,D,E,F)
     COMMON/AAA/ VDRC,VDRI,VDRF,PI,PF
     A = Al * PI - A2 * PF
     B = B1 * PI - B2 * PF
     C = C1 * PI - C2 * PF
     D = Dl * PI - D2 * PF
     E = E1 * PI - E2 * PF
     F = F2 * PF - F1 * PI
     RETURN
     END

     SUBROUTINE GAUSSJ
     INCLUDE 'PI.INC'
     COMMON /CCC/A(N,NPM)
     DATA DTM/l./,EPS/1.E-10/
     DO 40 K = 1,N
     DTM = DTM * A(K,K)
     IF (DABS(A(K,K)) .GT. EPS) GO TO 10
     WRITE (6,50)
     CALL EXIT
10   KP1 = K + 1
     DO 20 J = KP1,NPM
20   A(K,J) = A(K,J) / A(K,K)
     A(K,K) = 1.
     DO 40 I = 1,N
     IF (I .EQ. K .OR. A(I,K) .EQ. 0.) GO TO 40
     DO 30 J = KP1,NPM
30   A(I,J) = A(I,J) - A(I,K) * A(K,J)
     A(I,K) = 0.
40   CONTINUE
     RETURN
50   FORMAT (' SMALL PIVOT - MATRIX MAY BE SINGULAR')
     END

     SUBROUTINE RDWRT (NP)
     COMMON/AAA/ VDRC,VDRI,VDRF,PI,PF
     GO TO (10,30,20) NP
10   WRITE (6,50)
     READ (5,60) VDRC
     RETURN
20   WRITE (6,70)
     READ (5,60) VDRI
```

```
30    WRITE (6,70)
      READ (5,60) PI
      IF (NP .EQ. 2) GO TO 40
      WRITE (6,90)
      READ (5,60) VDRF
40    WRITE (6,100)
      READ (5,60) PF
      RETURN
50    FORMAT (' TOTAL VOLUME OF DISK REPLACED WITH CORE IN CC OR CI = ')
60    FORMAT (F20.0)
70    FORMAT (' TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN ',
     *  ' THE SYSTEM'/' FROM WHICH EXPANSION IS MADE - IN',
     *  ' CC OR CI = ')
80    FORMAT (' INITIAL PRESSURE IN PSIA = ')
90    FORMAT (' TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN ',
     *  ' THE SYSTEM'/' INTO WHICH EXPANSION IS MADE - IN',
     *  ' CC OR CI = ')
100   FORMAT (' FINAL EXPANSION PRESSURE IN PSIA = ')
      END

      SUBROUTINE HOUSE (IP)
      DO 40 I=1,3
      IF (IP .EQ. 1) GO TO (10,20,30) I
      IF (IP .EQ. 2) GO TO (30,20,10) I
10    WRITE (6,50)
      GO TO 40
20    WRITE (6,60)
      GO TO 40
30    WRITE (6,70)
40    CONTINUE
50    FORMAT (5X,'*',65X,'*')
60    FORMAT (5X,'*',33(' *'))
70    FORMAT (/)
      RETURN
      END

      SUBROUTINE STDMV (ND,AMEAN,SD,VAR)
      INCLUDE 'PI.INC'
      COMMON/BBB/ POR(MNDS)
      SUMX=O.
      SUMXSQ=O.
      DO 10 I = 1,ND
      SUMX = SUMX + POR(I)
10    SUMXSQ = SUMXSQ + POR(I)**2
      AN = FLOAT(ND)
      AMEAN = SUMX / AN
      IF (ND .EQ. 1) RETURN
```

```
      VAR = (AN*SUMXSQ-SUMX**2) / (AN*(AN-1.))
      SD = SQRT(VAR)
      RETURN
      END
      REAL FUNCTION VS (A,B,C,D,E)
      VS = A + B + C + D + E
      END

      REAL FUNCTION VDRMG1 (A1,Bl,C1,D1,El,A2,B2,C2,D2,E2,F,G,H,VV1,VV2)
      VDRMG1 = F / G * VS (A1,B1,C1,D1,E1) - VS (A2,B2,C2,D2,E2) +
     *  H / G * (VVl + VV2)
      END
      REAL FUNCTION VDRMG2 (Al,B1,C1,D1,El,A2,B2,C2,D2,E2,F,G,H,VVl,VV2)
      VDRMG2 = (G * VS (A1,B1,C1,D1,E1) - F * VS (A2,B2,C2,D2,E2) -
     *  H * (VV1 + VV2)) / (F - G)
      END
```

POROS Example Run

```
POROS    RUN PART l OR PART 2 (TYPE IN 1 OR 2)

      ***** PART 1 *****
ENTER DATA SET NAME:  REF.VOL
VOLUME OF TOGGLE VALVE WHEN OPENED - CC OR CI  (V5) = O

EXPANSION NO. 1
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM FROM
WHICH EXPANSION IS MADE - IN CC OR CI =  7.095

INITIAL PRESSURE IN PSIA = 96.33

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM INTO
WHICH EXPANSION IS MADE - IN CC OR CI =  7.095

FINAL EXPANSION PRESSURE IN PSIA = 29.44

EXPANSION NO. 2
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM FROM
WHICH EXPANSION IS MADE - IN CC OR CI =  O

INITIAL PRESSURE IN PSIA = 96.34

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM INTO
WHICH EXPANSION IS MADE - IN CC OR CI =  14.19
```

FINAL EXPANSION PRESSURE IN PSIA = 32.19

EXPANSION NO. 3
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM FROM WHICH EXPANSION IS MADE - IN CC OR CI = O

INITIAL PRESSURE IN PSIA = 96.35

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM INTO WHICH EXPANSION IS MADE - IN CC OR CI = 21.285

FINAL EXPANSION PRESSURE IN PSIA = 33.73

EXPANSION NO. 4
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM FROM WHICH EXPANSION IS MADE - IN CC OR CI = O

INITIAL PRESSURE IN PSIA = 96.35

TOTAL VOLUME OF DISK REMOVED FROM THE SAMPLE CUP IN THE SYSTEM INTO WHICH EXPANSION IS MADE - IN CC OR CI = 33.701

FINAL EXPANSION PRESSURE IN PSIA = 47.56

I	VDRI	PI	VDRF	PF
1	7.095	96.330	7.095	29.440
2	0.000	96.340	14.190	32.190
3	0.000	96.350	21.285	33.730
4	0.000	96.350	33.701	47.560

A(1,1)...A(4, 9)

66.89	66.89	-29.44	-29.44	-474.58	1.00	0.00	0.00	0.00
-32.19	64.15	64.15	-32.19	456.78	0.00	1.00	0.00	0.00
-33.73	62.62	-33.73	62.62	717.94	0.00	0.00	1.00	0.00
-47.56	48.79	48.79	48.79	1602.82	0.00	0.00	0.00	1.00

A(1,1)...A(4, 9)

1.00	0.00	0.00	0.00	4.26	0.01	-0.01	-0.01	0.02
0.00	1.00	0.00	0.00	3.42	0.01	0.01	0.01	0.00
0.00	0.00	1.00	0.00	15.11	0.00	0.00	-0.01	0.02
0.00	0.00	0.00	1.00	18.48	0.00	-0.01	0.00	0.02

```
**********************************************************************************
*   DATA SET NAME : REF.VOL                                                      *
*   V1 = 4.263 CC OR CI                                                          *
*   V2 = 3.423 CC OR CI                                                          *
*   V3 = 15.108 CC OR CI                                                         *
*   V4 = 18.476 CC OR CI                                                         *
*   V5 = 0.000 CC OR CI                                                          *
*   (WHEN V5 IS PRINTED AS ZERO ABOVE, V1, V3 AND V4                             *
*    INCLUDES THEIR TOGCLE VALVE VOLUMES)                                        *
**********************************************************************************

RERUN PART 1 FOR NEW DATA SET (TYPE IN Y OR N) ? N CONTINUE TO RUN PART 2
(TYPE IN Y OR N) ? Y

     ***** PART 2 *****
V2 INCLUDED IN INITIAL VOLUME (TYPE IN Y OR N) ? Y ENTER CORE SAMPLE NAME
: 337-B
ENTER DATA SET NAME : 337-B01  TOTAL VOLUME OF DISK REPLACED WITH CORE IN
CC OR CI = 14.19  READ IN(R) OR COMPUTE(C) BULK VOLUME OF CORE (TYPE IN R OR
C) ? R  BULK VOLUME OF CORE IN CC OR CI = 12.87  RESIDUAL PRESSURE WITHIN THE
VACUUM SYSTEM = O  INITIAL PRESSURE IN PSIA = 96.36 FINAL EXPANSION PRESSURE
IN PSIA = 45.01  EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?

**********************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B01)                          *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                 *
*   PVAC = 0.00 PSIA      PI = 96.36 PSIA          PF = 45.01 PSIA               *
*   POROSITY = 0.329      (WITH VP = 4.236         VG = 8.634 CC OR CI)          *
*   (EXPANSION METHOD USED = 1                     V2INC = Y)                    *
**********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME :  337-B02
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.34
FINAL EXPANSION PRESSURE IN PSIA = 40.1
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  2

**********************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B02)                          *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                 *
*   PVAC = 0.00 PSIA      PI = 96.34 PSIA          PF = 40.10 PSIA               *
*   POROSITY = 0.324      (WITH VP = 4.168         VG = 8.702 CC OR CI)          *
*   (EXPANSION METHOD USED = 2                     V2INC = Y)                    *
**********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
```

```
ENTER DATA SET NAME :  337-B03
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.33
FINAL EXPANSION PRESSURE IN PSIA = 27.04
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  3

*********************************************************************************
*   CORE SAMPLE NAME : 337-B   (DATA SET NAME : 337-B03)                        *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                *
*   PVAC = 0.00 PSIA      PI = 96.33 PSIA          PF = 27.04 PSIA              *
*   POROSITY = 0.319      (WITH VP = 4.100         VG = 8.770 CC OR CI)         *
*   (EXPANSION METHOD USED = 3                     V2INC = Y)                   *
*********************************************************************************
RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME :  337-04
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.36
FINAL EXPANSION PRESSURE IN PSIA = 58.4
XPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  4

*********************************************************************************
*   CORE SAMPLE NAME : 337-B   (DATA SET NAME : 337 04 )                        *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                *
*   PVAC = 0.00 PSIA      PI = 96.36 PSIA          PF = 58.40 PSIA              *
*   POROSITY = 0.335      (WITH VP = 4.311         VG = 8.559 CC OR CI)         *
*   (EXPANSION METHOD USED = 4                     V2INC = Y)                   *
*********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME · 337-B05
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.39
FINAL EXPANSION PRESSURE IN PSIA = 65.43
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  5

*********************************************************************************
*   CORE SAMPLE NAME : 337-B   (DATA SET NAME : 337-Bos)                        *
*   VB = 12.870 cc OR CI   VDRC = 14.190 cc OR CI                               *
*   PVAC = 0.00 PSIA      PI = 96.39 PSIA          PF = 65.43 PSIA              *
*   POROSITY = 0.345      (WITH vp = 4.446         VG = 8.424 cc OR CI)         *
*   (EXPANSION METHOD USED = 5                     V2INC = Y)                   *
*********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ? Y
ENTER DATA SET NAME :  337-B06
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.37
```

```
FINAL EXPANSION PRESSURE IN PSIA = 63.5l
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  6

*****************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B06)                     *
*   VB = 12.870 cc OR CI   VDRC = 14.190 cc OR CI                           *
*   PVAC = 0.00 PSIA       PI = 96.37              PSIA PF = 63.51 PSIA     *
*   POROSITY = 0.311       (WITH vp = 4.005        VG = 8.865 cc OR CI)     *
*   (EXPANSION METHOD USED = 6                     V2INC = Y)               *
*****************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME :  337-B07
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.43
FINAL EXPANSION PRESSURE IN PSIA = 67.09
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  7

*****************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B07)                     *
*   VB = 12.870 cc OR CI   VDRC = 14.190 cc OR CI                           *
*   PVAC = 0.00 PSIA       PI = 96.43 PSIA         PF = 67.09 PSIA          *
*   POROSITY = 0.310       (WITH VP = 3.994        VG = 8.876 CC OR CI)     *
*   (EXPANSION METHOD USED = 7                     V2INC = Y)               *
*****************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME :  337-B08
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM - 0
INITIAL PRESSURE IN PSIA = 96.37
FINAL EXPANSION PRESSURE IN PSIA = 38.18
EXPANSION METHOD USED (TYPE IN l,2,3,4,5,6,7,8,9 OR lO) ?  8

*****************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B08)                     *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                            *
*   PVAC = 0.00 PSIA PI = 96.37 PSIA PF = 38.18 PSIA                        *
*   POROSITY = 0.325 (WITH VP = 4.183 VG = 8.687 CC OR CI)                  *
*   (EXPANSION METHOD USED = 8 V2INC = Y)                                   *
*****************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ? Y
ENTER DATA SET NAME :  337-B09
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.43
FINAL EXPANSION PRESSURE IN PSIA = 45.25
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ? 9
```

```
**********************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B09)                          *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                 *
*   PVAC = 0.00 PSIA      PI = 96.43 PSIA          Pf = 45.25 PSIA               *
*   POROSITY = 0.317      (WITH VP = 4.078         VG = 8.792 CC OR CI)          *
*   (EXPANSION METHOD USED = 9                     V2INC = Y)                    *
**********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  Y
ENTER DATA SET NAME :  337-BlO
RESIDUAL PRESSURE WITHIN THE VACUUM SYSTEM = O
INITIAL PRESSURE IN PSIA = 96.43
FINAL EXPANSION PRESSURE IN PSIA = 76.53
EXPANSION METHOD USED (TYPE IN 1,2,3,4,5,6,7,8,9 OR 10) ?  10

**********************************************************************************
*   CORE SAMPLE NAME : 337-B  (DATA SET NAME : 337-B10)                          *
*   VB = 12.870 CC OR CI  VDRC = 14.190 CC OR CI                                 *
*   PVAC = 0.00 PSIA      PI - 96.43 PSIA          PF = 76.53 PSIA               *
*   POROSITY = 0.314      (WITH VP = 4.040         VG = 8.830 CC OR CI)          *
*   (EXPANSION METHOD USED =10                     V2INC = Y)                    *
**********************************************************************************

RERUN FOR SAME CORE WITH DIFFERENT DATA SET (TYPE IN Y OR N) ?  N

**********************************************************************************
*   SUMMARY (CORE SAMPLE NAME : 337-B)                                           *
*   POR (337-B01 ) = 0.329                                                       *
*   POR (337-B02 ) = 0.324                                                       *
*   POR (337-B03 ) = 0.319                                                       *
*   POR (337-04  ) = 0-335                                                       *
*   POR (337-B05 ) = 0.345                                                       *
*   POR (337-B06 ) = 0.311                                                       *
*   POR (337-B07 ) = 0.310                                                       *
*   POR (337-B08 ) = 0.325                                                       *
*   POR (337-B09 ) = 0.317                                                       *
*   POR (337-B10 ) = 0.314                                                       *
*   POROSITY(MEAN) = 0.323                                                       *
*   STANDARD DEVIATION = 0.011          (VARIANCE = 0.000)                       *
**********************************************************************************

RUN FOR NEW CORE SAMPLE (TYPE IN Y OR N) ?  N
```

PROGRAM : POROS - PC VERSION/INTERACTIVE MODE

AUTHOR : HWI W. BANG
DATE : AUGUST 1989
O&G, ISGS

INTRODUCTION

PART 1: COMPUTES REFERENCE VOLUMES OF THE TEMCO'S HELIUM POROSIMETER SYSTEM INCLUDING V1,V2,V3,V4 AND V5(SEE PART 1 OF GLOSSARY), USING THE EXPANSION METHODS DISCUSSED IN PART 1 OF INPUT BELOW

RUN (1) EVERY TIME UPON REPLACING TUBING,VALVE OR REFERENCE CHAMBERS
(2) ROUTINELY TO CHECK VOLUME REDUCTION BY DIRT OR MOISTURE IN THE SYSTEM
(3) AFTER SET OF MEASUREMENTS, CALIBRATE THE REFERENCE VOLUMES IN ACCORDANCE WITH INSTRUCTIONS IN PART 1 OF INPUT BELOW

PART 2: COMPUTES GRAIN VOLUME, PORE VOLUME AND POROSITY USING UPTO 10 DIFFERENT EXPANSION METHODS(SEE AN OPTION KEY, EXPNSN, BELOW)

ALLOWS UP TO 30 MEASUREMENTS PER CORE SAMPLE PER RUN AND DETERMINES MEAN POROSITY AND STANDARD DEVIATION OF THE METHOD

OPTION KEYS

RNEWDATA: DETERMINES WHETHER TO RERUN PART 1 OR PART 2 FOR NEW DATA
= Y : RERUNS FOR NEW DATA SET
= N : TRANSFERS TO RNEWCORE OR RUNCONT

RNEWCORE: DECIDES WHETHER TO RERUN PART 2 FOR NEW CORE SAMPLE = Y : RUNS FOR NEW CORE SAMPLE
= N : RERUNS FOR SAME SAMPLE WITH DIFFERENT DATA SET

PART12 : SELECTS WHAT PART OF THE PROGRAM TO RUN
= 1 : RUNS PART 1 WITH OPTION TO CONTINUE TO RUN PART 2
= 2 : RUNS PART 2 OF THE PROGRAM (INPUT AS AN INTEGER CONSTANT)

RUNCONT : DECIDES WHETHER TO CONTINUE TO RUN THE PROGRAM
= Y : CONTINUES RUNNING
= N : TERMINATES RUNNING

RCVB : CHOOSES TO READ IN OR COMPUTE BULK VOLUME OF CORE SAMPLE
= R : READS IN BULK VOLUME
= C : COMPUTES BULK VOLUME

EXPNSN : LINKS TO THE STATEMENT NO. FOR THE EXPANSION METHOD USED (INPUT AS AN INTEGER CONSTANT / USED IN PART 2)
= 1 : ST NO 130 - SAMPLE CUP TO REFERENCE CHAMBER 1(RC 1)
= 2 : ST NO 140 - SAMPLE CUP TO REFERENCE CHAMBER 2(RC 2)
= 3 : ST NO 145 - SAMPLE CUP(SC) TO RC 1 + RC 2

= 4 : ST NO 150 - SC + RC 1 TO RC 2
= 5 : ST NO 155 - SC + RC 2 TO RC 1
= 6 : ST NO 160 - RC 1 TO SC
= 7 : ST NO 170 - RC 2 TO SC
= 8 : ST NO 180 - RC 1 TO RC 2 + SC
= 9 : ST NO 190 - RC 2 TO RC 1 + SC
=10 : ST NO 200 - RC 1 + RC 2 TO SC

V2INC : DETERMINES WHETHER TO INCLUDE VOLUME OF COMMON LINES(V2) IN TOTAL INITIAL VOLUME OF THE SYSTEM FROM WHICH EXPANSION IS MADE (SEE PART 1 OF GLOSSARY BELOW)
= Y : V2 INCLUDED
= N : V2 EXCLUDED

GLOSSARY

PART 1

DATANAME : DATA SET NAME(FOR IDENTIFICATION PURPOSE)
USED IN ARRAY, DN(MNDS) AND POR(DN'S) IN OUTPUT SUMMARY

N : NUMBER OF UNKNOWNS
EX. PARAMETER (N=4,.....) IN 'PI.INC'
PARAMETER (N=5,.....) IN 'PI.INC'

V1 : VOLUME OF LINE BETWEEN SAMPLE VALVE $ cup FILLED WITH DISKS
V2 : VOLUME OF COMMON LINES
V3 : VOLUME OF REFERENCE CHAMBER 1
V4 : VOLUME OF REFERENCE CHAMBER 2
V5 : VOLUME OF TOGGLE VALVE WHEN OPENED

PV : RESIDUAL PRESSURE IN-THE VACUUM SYSTEM INTO WHICH EXPANSION IS MADE(PSIA)

VV : ANY CHAMBER VOLUME(S) WITHIN THE VACUUM SYSTEM INTO WHICH EXPANSION IS MADE(CC OR CI)

PI : INITIAL PRESSURE (PSIA)

PF : FINAL EXPANSION PRESSURE (PSIA)

VDR : TOTAL VOLUME OF DISK REMOVED - VARIABLE (cc OR CI)

SPECIFICATIONS

DISK	DIAMETER		HEIGHT		VOLUME	
(NO)	(CM)	(IN)	(CM)	(IN)	(CC)	(CI)
1	2.667	1.050	0.318	0.125	1.774	0.108
2	2.667	1.050	0.953	0.375	5.321	0.325
3	2.667	1.050	1.270	0.500	7.095	0.433
4	2.667	1.050	2.223	0.875	12.416	0.758
5	2.667	1.050	2.778	1.107	15.519	0.947

VDRC : TOTAL VOLUME OF DISK REPLACED WITH CORE SAMPLE - (CC OR CI)

VDRI : VDR IN THE SYSTEM FROM WHICH EXPANSION IS MADE - (CC OR CI)
VDRF : VDR IN THE SYSTEM INTO WHICH EXPANSION IS MADE - (CC OR CI)

PART 2

CORENAME : CORE SAMPLE NAME(FOR IDENTIFICATION PURPOSE)
DC : DIAMETER OF CORE SAMPLE(CM OR IN)
HC : HEIGHT OF CORE SAMPLE(CM OR IN)
PV, PI, PF : SEE PART 1
VDRC, vv : SEE PART 1
VB : BULK VOLUME OF CORE SAMPLE(CC OR CI)
VG : GRAIN VOLUME OF CORE SAMPLE(CC OR CI)
VP : PORE VOLUME OF CORE SAMPLE(CC OR CI)
POR : POROSITY(FRACTION)
NDS : TOTAL NUMBER OF DATA SETS FOR A GIVEN CORE SAMPLE, CONCERNING POR AND DN
NOTE : MAX NO OF NDS, I.E., MNDS IS SET EQUAL TO 30 IN 'PI.INC'. MODIFY MNDS, IF NECESSARY
POREMEAN : MEAN POROSITY
STDV : STANDARD DEVIATION
VAR : VARIANCE

INPUT
GENERAL
* UNITS FOR INPUT DATA SET SHOULD BE CONSISTENT, I.E., CM WITH CC(CU CM) OR IN WITH CI(CU IN)
READ PART12 - (INTEGER CONSTANT WITHIN 20 COLUMNS)
READ DATANAME - (ANY COMBINATION OF CHARACTER AND CONSTANT UPTO 8 COLUMNS)
READ CORENAME - (
READ RUNCONT - (TYPE IN Y OR N WITHIN 8 COLUMNS)
READ RNEWCORE - (
READ RNEWDATA - ('

PART 1

READ V5 - (F20.0), ONLY IF N = 4

* IMPORTANT *
THE FOLLOWING ORDER OF EXPANSION SHOULD BE MADE WITH VARYING VDR
(1) SC TO RC 1+RC 2 (EX. VDRI=VDRF=7.095 CC - DISK 3)
(2) RC 1 TO SC+RC 2 (EX. VDRI=0 VDRF=14.190 CC - DISKS 3+3)
(3) RC 2 TO SC+RC 1 (EX. VDRI=O VDRF=21.285 - DISKS 1+2+3+3)
(4) RC 1+RC 2 TO SC (EX. VDRI=O VDRF=33.701 - DISKS 1+2+3+3+4)
(5) SC+RC 1 TO RC 2 (EX. VDRI=VDRF=42.125 - DISKS 3+3+4+5)

* NOTE*
INPUTTING V5 WITH N=4 IN 'PI.INC' AND V2INC=Y IS RECOMMENDED

(1) V5 IS UNKNOWN : SET V5 = 0.0 AND SOLVE 4 SIMULTANEOUS EQUATIONS FOR 4 UNKNOWNS - V1+V5, V2, V3+V5 AND V4+V5 (V2INC = Y ONLY)
(2) V5 = KNOWN : SET V5 = KNOWN VALUE. 4 UNKNOWNS - V1, V2, V3 AND V4 (V2INC = Y OR N)

V5 MAY BE COMPUTED ALONG WITH V1, V2, V3, AND V4 WITH N=5 IN 'PI.INC'. IN SUCH A CASE, IT IS ESSENTIAL TO OBTAIN ACCURATE PRESSURE DATA, SINCE V5 IS A SMALL VOLUME LESS THAN 0.5 CC

SIMULTANEOUS EQUATIONS FOR 4 OR 5 UNKNOWNS IN MATRIX FORM ARE A(I,J) B(I) = RHS(I) WHERE A(I,J) IS A MATRIX FOR I=1,N WITH

INDEX	INPUT	OUTPUT
J=1,N	COEFFICIENT MATRIX	IDENTITY MATRIX
J=M(N+1)	RHS(I)	SOLUTION VECTOR, B(I)
J=M+1,N+M	IDENTITY MATRIX	INVERSE OF COEFF MATRIX

READ VDRI - (F20.0)
READ PV - (F20.0)
READ PI - (F20.0)
READ VDRF - (F20.0)
READ PF - (F20.0)

PART 2

READ V1 - (F20.0)
READ V2 - (F20.0)
READ V3 - (F20.0)
READ V4 - (F20.0)
READ V5 - (F20.0)
READ RCVB - (TYPE IN R OR C WITHIN 8 COLUMNS)
READ VB - (F20.0)
READ VDRC - (F20.0)
READ DC - (F20.0)
READ HC - (F20.0)
READ PV - (F20.0)
READ PI - (F20.0)
READ PF - (F20.0)
READ V2INC - (TYPE IN Y OR N WITHIN 8 COLUMNS)

READ EXPNSN - (INTEGER CONSTANT WITHIN 20 COLUMNS)
OUTPUT

PART 1

NUMERICAL PARAMETERS AND COPY OF INPUT DATA
COPY OF INPUT AND OUTPUT A(I,J) - SEE GLOSSARY ABOVE
Vl THRU V5 (V1,V3 AND V4 MAY INCLUDE V5, IN CASE V5=0.)

PART 2

COPY OF V1 THRU V5

CORE DIMENSIONS,BULK VOLUME, AND INITIAL AND FINAL PRESSURES
POROSITY WITH PORE VOLUME, GRAIN VOLUME, EXPANSION METHOD USED AND V2INC

RUNNING THE PROGRAM

* NOTE *

ASSIGN AN APPROPRIATE VALUE TO N IN 'PI.INC' BEFORE COMPILING/LINKING THE PROGRAM(REQUIRED ONLY IF V5 IS TO BE COMPUTED, I.E., N=5)

IT IS RECOMMENDED TO SET V2INC=Y SO THAT ACCURATE PRESSURE READING CAN BE USED IN THE COMPUTATION(TEMCO'S HELIUM POROSIMETER CAN NOT ACCURATELY READ INCREASED CHAMBER PRESSURE UPON CLOSING TOGGLE VALVE) LOCK CAPS LOCK KEY FOR PROPER USE OF OPTION KEYS IN THE PROGRAM

(1) TYPE IN POROS FOLLOWED BY ENTERING RETURN KEY

(2) FOLLOW STEP-BY-STEP INSTRUCTIONS(USER INTERACTIVE MODE)

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Measure effective porosity on core samples for use in engineering and geological analyses

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Porosimetry	By field or project, e.g. Energy Field or MCA study	in publications	Various disks (Haggerty)	Engineering PCs

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

GAS PERMEAMETER

Dennis J. Haggerty

Scope and Use of the Method

The gas permeameter is used to determine the gas or air permeability of core samples. The permeameter is Temco's GP-D series Model GP-13-101-D equipped with a Hassler-type core holder, gas flow meters and a differential pressure transducer. The accuracy of the method is limited primarily by the calibration of the differential pressure transducer and flowmeter. The method has been tested for a sintered metal core sample. This is a common method for measuring gas permeability, and is often used in core analyses.

General Principles

Gas is injected through the cylindrical core sample in a Hassler-type core holder. Confining pressure can be applied on the core sample using either a hydraulic pump or an exterior regulated gas reservoir. The pressure drop across the core sample is measured with an electronic differential pressure transducer. The gas flow rate is measured up to 1700 ccpm with three calibrated flowmeters. Using the measured differential pressure and gas flow rates, the gas permeability can be calculated using Darcy's equation for isothermal, steady-state flow. Additional data required are gas viscosity and core dimensions. The pressure transducer requires recalibration once a month, or as often as required, using a dead weight tester. The equipment has three factory calibrated flowmeters (rotameters) for low, medium and high ranges. If the gas permeability is to be measured at reservoir conditions, a hydraulic pump should be used to obtain the desired confining pressure. Otherwise, for a routine procedure a regulated gas cylinder of nitrogen or helium can be used to apply confining pressure (recommended at 200 psig). Calculations for gas permeability and the linearity check plot for the experimental data points can be performed on a PC in user-oriented Fortran 77 program, PERMG, in an interactive mode.

Equipment and Apparatus

Temco's GP-13-101-D gas permeameter is equipped with Temco's RCH-1 Hassler type core holder, three Cole-Parmer type gas flowmeters, Validyne's DP-15 electronic differential pressure transducer, Validyne's CD 101 signal conditioner, Newport Electronics' Q200 digital display and metering valves. In addition, a regulated gas cylinder of nitrogen or helium and a hydraulic pump are required. Figure 2 shows the flow diagram of the gas permeameter.

Procedure

1. Close all valves (including rotameters) on the instrument.

2. Load the core sample into the core holder (note 1).

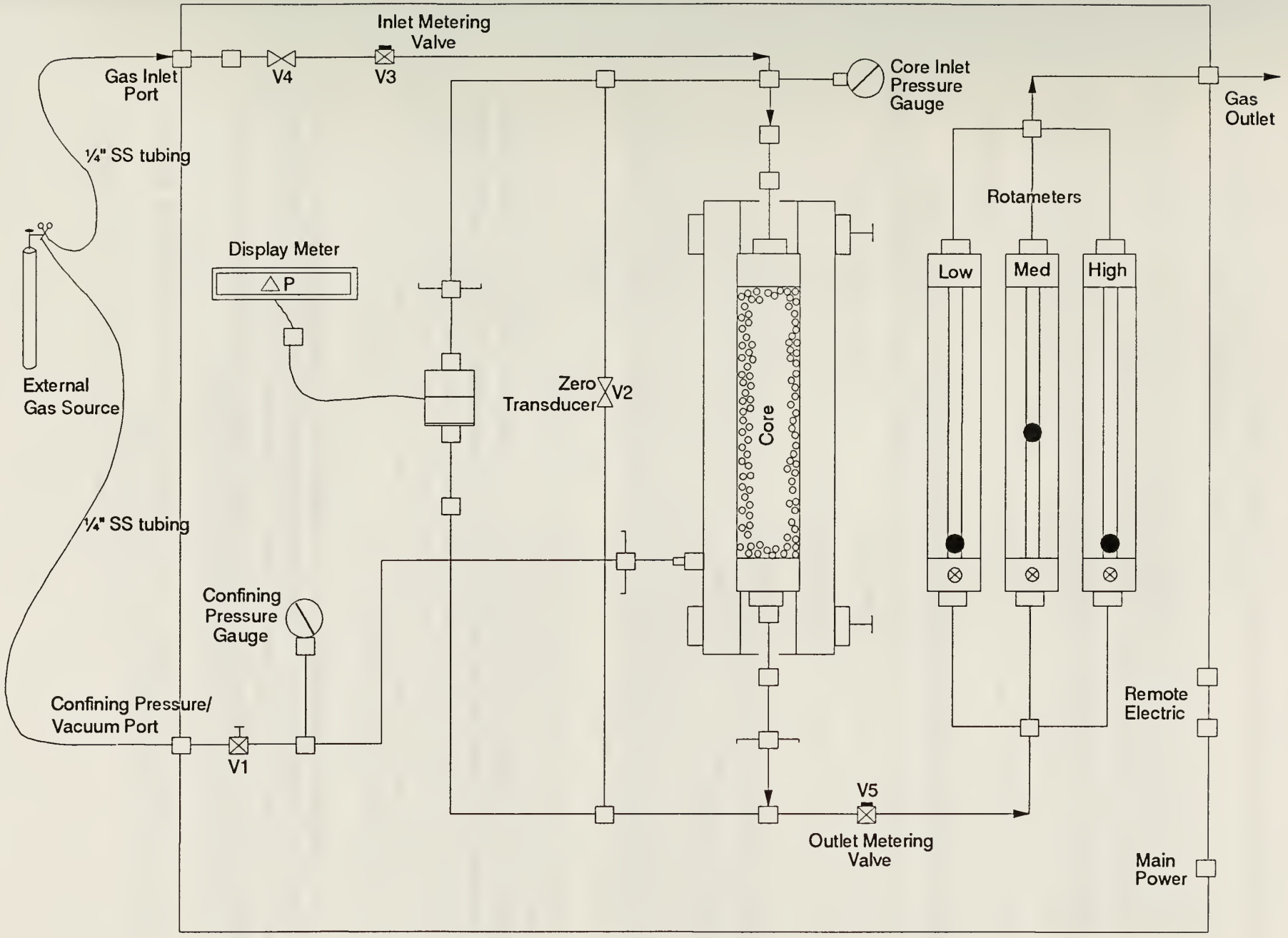


Figure 2. Flow Diagram of Gas Permeameter

SOP-2

3. Turn on the instrument and allow 30 minutes to warm up.

4. Open the zero transducer valve, V2 (the LED display should read zero).

5. Slowly and carefully open the confining pressure valve, V1, to obtain the desired pressure with the gas in the source cylinder or hydraulic pump (note 2).

6. After obtaining the desired confining pressure, close V1 (make sure that the source valve is also closed) and bleed down line pressure.

7. Open the downstream metering valve, V5 (note 3).

8. Open the main valve of the external gas source cylinder.

9. Open the labeled gas source valve with the pressure regulator (maintaining a lower pressure than the transducer plate limit).

10. Open the gas inlet valve, V4 to admit gas (note 4).

11. Slowly open the upstream metering valve, V3 to regulate gas rates.

12. Close V2 (note 5).

13. Observe the appropriate rotameter scale and record the scale reading and L, M, or H for the rotameter used (start with H and, if necessary, switch to M or L rotameter while closing the other two).

14. Record the differential pressure percentile reading (P%).

Note 1. Core sample installation: Slide the core sample through the ferrule and into the rubber sleeve. If the sample does not slide easily into the sleeve, a vacuum can be applied to the confining pressure port and this vacuum will enlarge the sleeve inner diameter. Install the distribution plug through the ferrule and against the core face. Next, install a spacer plug then screw the retainer into the end cap until the retainer is flush against the end cap. Finally, reconnect tube fittings to the coreholder body.

Note 2. If the gas permeability is to be determined at reservoir conditions, a hydraulic pump should be attached to the confining pressure/vacuum inlet. When the gas source is to be used to apply the confining pressure, attach the gas source to this inlet. Use the labeled confining pressure source valve close to the pressure regulator. In this case, it is recommended that the confining pressure be in the neighborhood of 100 psig.

Note 3. If the gas permeability is to be determined at atmospheric back pressure, V5 should be first fully open. Otherwise, V5 is partially closed.

Note 4. The gas inlet pressure should not exceed the sum of back pressure and the rated pressure for the diaphragm plate in the transducer.

Note 5. High upstream pressure or inadvertent pressure differentials will damage the ΔP diaphragm plates. Therefore, it is useful to leave the zero transducer valve in the open (up) position except when actually reading a P% value. Since the differential pressure transducer has an accuracy of 0.5% full scale, it is advantageous to measure ΔP in the higher percentile ranges. Thus, a lower ΔP plate, possibly 2.0, 3.2, or 5.0 psig would decrease the uncertainty of a given differential pressure value.

Calculations

Darcy's equation for linear, isothermal, steady-state flow of gas allows permeability, ka (md) to be calculated by the equation:

$$ka = \frac{2000\ \mu L P_b Q_b}{A(P_i^2 - P_o^2)} \quad (1)$$

Where μ is the viscosity of gas (cp), L is the core length (cm), A is the cross-sectional area of core (sq. cm), P_b is the base pressure (atm, mass flowmeter's calibration), Q_b is the volumetric flow rate measured at P_b (cc/sec), Pi is the upstream pressure (atm) and Po is the downstream pressure (atm). If the flow medium and atmospheric conditions are not those of the calibrated tables (air, 14.7 psia and 70°F), the actual flow rate Q may be estimated by the equation:

$$Q = Qsc[(f/p - 1)/(f/p_{sc} - 1)]^{0.5} \quad (2)$$

Where Qsc is the standard flow rate, f is the float density, p is the actual gas density at outlet conditions and p_{sc} is the gas density at standard conditions. Since Darcy's equation is valid for viscous flow, valid data points must lie on the straight line portion of a y versus x plot where y and x are defined as:

$$y = Q_b - P_b/A \quad (3)$$
$$x = (P_i^2 - P_o^2)/(2000 \cdot L) \quad (4)$$

for a given experimental run. The validity of measured data can be checked by a y versus x plot (fig. 3).

Example calculation: A sintered metal core with known ka = 51.5 md has the following data:

L = 2.54 cm
A = 5.09 cm^2

Additional data pertinent to the measurements are:

μ = 0.01812cp (for air)
P_b = 1 atm
Po = 1 atm
Rated pressure of diaphragm plate for 100% full scale = 5 psig
confining pressure = 200 psig
Assumption: μ of Nitrogen = μ of air

Measured data

Run No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Rotometer reading*	46	35	26	76	59	125	142
ΔP%	23.6	18.6	13.8	43.8	32.1	86.9	98.6

---

*medium scale

Results

Run No.	**Q(cc/sec) 1**	**P(atm) 2**	**ka(md) 3**	**y 4**	**x 5**
1	0.453	1.0803	49.059	0.089	0.32872E-04
2	0.338	1.0622	46.827	0.066	0.25696E-04
3	0.255	1.0469	47.996	0.050	0.18914E-04
4	0.900	1.1490	50.838	0.177	0.63022E-04
5	0.612	1.1092	48.060	0.120	0.45332E-04
6	1.912	1.2956	50.960	0.376	0.13357E-04
7	2.271	1.3354	52.437	0.446	0.15418E-04

Computational Procedure

Column 1 - from flowmeter calibration data (cc/min). Convert to cc/sec{cc/min/60}.
Column 2 - Pi = Po + (ΔP%)(5 psig)/14.7 psi
Column 3 - from equation 1
ka mean = 49.787 md
standard deviation = 1.705
Column 4 - from equation 3
Column 5 - from equation 4

The linearity of Figure 3 (plot of x vs y) confirms the validity of these measurements.

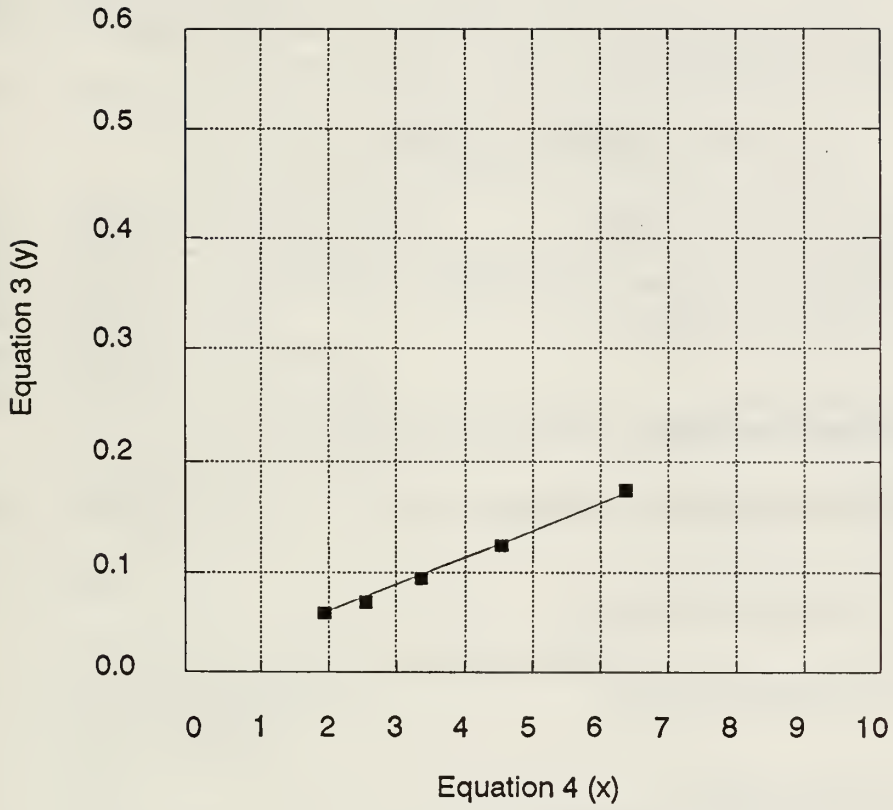


Figure 3. A plot of flowrate (base pressure over area) against pressure difference per length (Values times 10^{-5}).

Accuracy

The accuracy of this instrument is limited by the calibration of the differential pressure transducer within 0.5% of full scale and gas flow meters within 2% of full scale.

The accuracy of the differential pressure transducer may be improved by using a lower ΔP plate, since it would decrease the uncertainty of a given differential pressure value. The accuracy of the method should be checked by confirmation of a linear distribution of data points on a y versus x plot as described by equations 3 and 4. Also, a lower ΔP plate would minimize turbulent flow effect. However, a higher ΔP plate is necessary to determine permeability values less than 3 millidarcies.

Fortran Program - PERMG

```
      AUTHOR : HWI W.(WAYNE) BANG
      DATE : FEBRUARY 1990
      OIL AND GAS, ISGS
      COMPUTES GAS PERMEABILITY

      CHARACTER*10 OUTDAT
      REAL*8 L,NDUM,KAMEAN,KA
      COMMON KA(15)
      DIMENSION DPP(15),QB(15),Y(15),X(15)
      DATA ATM/14.7/
      WRITE (6,108)
      READ (5,100) L,D,VISG,PB,PO,PDMX
      I=1
10    READ (5,100) DPP(I),QB(I),NDUM
      N=I
      I=I+1
      IF (NDUM .EQ. O) GO TO 10
      WRITE (6,101) L,D,VISG,PB,PO,PDMX
      WRITE (6,102)
      A=3.14159*(D/2.)**2
      DO 20 I=1,N
      Q=QB(I)/60.
      PIN=PO+PDMX*DPP(I)/100./ATM
      DPS=PIN**2-PO**2
      KA(I)=2000.*VISG*L*PB*Q/(A*DPS)
      Y(I)=Q*PB/A
      X(I)=DPS/(2000.*L)
20    WRITE (6,103) I,DPP(I),Q,PIN,KA(I)
      CALL SDM(N,KAMEAN,SD)
      WRITE (6,109) KAMEAN,SD
```

```
      WRITE (6,104)
      WRITE (6,105)
      READ (5,106) OUTDAT
      OPEN (UNIT=60,FILE=OUTDAT)
      DO 30 I=1,N
 30   WRITE (60,107) Y(I),X(I)
      STOP
100   FORMAT (6F10.0)
101   FORMAT (//lX,'  L  = ',F7.3,3X,'  D  = ',F7.3,4X,'VISG = ',F7.3/
     *        1X,'  PB = ',F7.3,3X,'  PO = ',F7.3,4X,'PDMX = ',F7.3)
102   FORMAT (/3X,'I',3X,'DPP(I)',4X,'QB(I)',4X,'PIN(I)',4X,'KA(I)'/
     *        3X,'-',3X,6(1H-),4X,5(1H-),4X,6(1H-),3X,7(1H-)/
              3X,' ',4X,'(%)',6X,'(CPS)',4X,'(ATM)',6X,'(MD)')
103   FORMAT (I4,3F9.3,F11.3)
104   FORMAT (/3X,'SEE OUTPUT FILE FOR Y(I) AND X(I)')
105   FORMAT (1X,'ENTER OUTPUT DATA FILE NAME FOR PLOT : ')
106   FORMAT (A)
107   FORMAT (F7.3,E15.5)
108   FORMAT (1X,' 1 2 3 4                                          5',
     * ' .....',/1X,'123456789012345678901234567890123456789',
     * '12345678901 .....'/)
109   FORMAT (35X,7(1H-)/25X,'MEAN KA = ',F7.3,' (STANDARD DEVIATION ',
     *      F6.3,')')
      END

      SUBROUTINE SDM (N,KAMEAN,SD)
      AL*8 KA,KAMEAN
      MMON KA(15)
      =O .
      SQ=0.
      =FLOAT(N)
       10 I=1,N
      =SX+KA(I)
10    SXSQ=SXSQ~KA(I)**2
      MEAN=SX/AN
       (AN .EQ. 1.) RETURN
      =SQRT((AN*SXSQ-SX**2)t(AN*(AN-1.)))
      TURN
      D
```

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Measure permeability in core samples.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Permeametry	By field or project, e.g. Energy Field or MCA study	in publications	Various disks (Haggerty)	Engineering PCs

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

Set Up

To set up the Mini-Permeameter, open the valve on the nitrogen tank and switch the power on. The gas regulator valve is turned clockwise until a predetermined pressure is reached on the gauge while the handle trigger is pressed and the probe tip plugged using a finger. This can be verified by the following steps. Pull the handle trigger and let the gas escape (the pressure will return to an atmospheric reading, record for use in calculations). Again, hold the probe against something that will not allow flow (a finger) and adjust the regulator until the maximum pressure desired is reached (25 psia is common). Often it is necessary to lower it by turning the regulator knob counter-clockwise.

Flow Meters

The three gas flow meters are connected in parallel, each one covering a different range. The digital readouts for each meter have their range written on them which tells the operator if a displayed number is valid (i.e. within its range). For instance, if the small meter has a range of 0-20 cubic centimeters per minute (ccpm), a reading of 21 ccpm is incorrect and the operator should use the medium-range meter. The medium range meter is accurate between 20 and 500 ccpm, and the high range meter is valid between 500 and 2000 ccpm. These flow readings are recorded along with a corresponding pressure from the LED meter.

Example Calculation

MODIFIED DARCY G_o EQUATION

$Ka = (2*\mu*Q)/[(a*G_o*(Pf^2-Pa^2)]$

WHERE: Ka = Air Permeability, Darcys

μ = Gas viscosity, centipoise

Q = Flow rate, cubic centimeters per minute(ccpm)

a = Internal diameter of probe tip, centimeters

G_o = Geometric factor, dimensionless

P_f = Final stabilized pressure, atmospheres

P_a = Measured atmospheric pressure, atmospheres

GIVEN:

μ = 0.177 centipoise @ 73°F

a = 0.3175 cm

G_o = 5.1 from Figure 4 based on the ratio between probe size and sample size (considered the half-space solution)

MINI-PERMEAMETER

Dennis J. Haggerty

The Temco Mini-Permeameter is used to determine the gas permeability of a rock sample. The concept is to force nitrogen into the rock sample while monitoring pressure and flow rate. With a modification of Darcy's law, gas permeability can be calculated for isothermal, steady-state gas flow.

The mini-permeameter was invented to generate permeability data quickly and inexpensively. The first mini-permeameter was used by Dykstra, et al, in 1950, but was limited by its size and awkwardness. Modern technological improvements have made the mini-permeameter practical for outcrop studies. Depositional patterns can be compared with permeability patterns and the existence of trends can be investigated. Outcrop permeability distribution studies are also conducted to generate the high volumes of data needed to successfully run modern simulators.

Description

The Temco Mini-Permeameter is equipped with gas flow meters, an electronic pressure gauge, a 9-volt battery, a 1-liter nitrogen bottle, a probe and teflon tubing. The unit is housed in a durable, water-proof carrying case and weighs roughly thirty pounds. The battery requires recharging after about 4 hours and a full nitrogen tank lasts about 6 hours under normal operating conditions.

Theory

The probe tip, made from pliable tubing (Tygon), is held firmly against the rock being measured and must form a tight seal. At the same time, the trigger on the probe handle is squeezed to inject nitrogen into the rock. When both the rotameter and the pressure gauge stabilize, the flow rate and the pressure are recorded and permeability to gas can be calculated for that point. The probe is then moved to the next surface and the process repeated. Sandstones only require a probe diameter of about one-eighth of an inch, whereas carbonates with much larger pore throats may require a probe diameter up to an inch.

Precision of the mini-permeameter can only be verified by its single point repeatability. The accuracy is established by comparing the results with the core plug air permeability (gas permeability), a difference of 10% can be common due to heterogeneity within the diameter of the plug. Measurements of (1 inch diameter) plug permeability and plug center-point mini-permeability show good agreement between 10 and 100 millidarcys. A set of standards cintered plugs is used for ideal correlation.

WHERE :

a = Internal diameter of probe tip, cm
b = external diameter of probe tip, cm
rcore = radius of cylindrical core, cm
lcore = length of cylindrical core, cm
R_D = rcore/a
L_D = lcore/a
b_D = b/a

Typical values for the above are:
a = 0.3175 cm (1/4 inch tubing)
b = 0.635 cm (1/4 inch tubing)
rcore = 5 cm
lcore = 2.54 cm

So:
R_D = 8
L_D = 15.75
b_D = 2

Therefore $G(b_D) = G_o = 5.1$

MEASURED:

Q = 350 ccpm
Pf = 18.7 psia
Pa = 14.4 psia

$$Ka = \frac{2 * 0.0177 * (350 / 60)}{0.3175*5.1*((18.7/14.696)^2-(14.4/14.696)^2)}$$

Ka = 0.194 Darcys

A computer program was written to rapidly compute the above equation. Lotus 123® is recommended to tabulate large numbers of points.

This Program Calculates Gas Permeability
from Minipermeameter Data

WRITTEN BY DENNIS J. HAGGERTY
ILLINOIS STATE GEOLOGICAL SURVEY
LANGUAGE - QUICKBASIC v4.5

```
CLS
3 PRINT
5 INPUT "ENTER ATMOSPHERIC PRESSURE: ", PI
6 FOR I = 1 TO 2
7 PRINT
10 INPUT "ENTER FINAL PRESSURE: ", PF
15 IF PF = 0 THEN 199
20 X = (PF / 14.7) ^ 2
30 Y = (PI / 14.7) ^ 2
40 XN = X - Y
50 XM = 5.1 * XN * .3175
60 PRINT
70 T1 = 2! * .0177 / 60
80 INPUT "ENTER FLOWRATE: ", FR
90 T2 = FR * T1 * 1000
100 XMD(I) = T2 / XM
105 XXMD = XMD(1) + XMD(2)
110 PRINT "THE PERMEABILITY IS: ", XMD(I), "MILLIDARCIES"
120 PRINT
135 NEXT I
137 XMD = XXMD / 2
138 PRINT XMD
140 GOTO 5
199 END
```

THE FOLLOWING IS AN EXAMPLE PRINTOUT:

```
ENTER ATMOSPHERIC PRESSURE:  14.4

ENTER FINAL PRESSURE:  18.7

ENTER FLOWRATE:  350
THE PERMEABILITY IS:          193.6173      MILLIDARCIES

ENTER FINAL PRESSURE:  18.7

ENTER FLOWRATE:  1200
THE PERMEABILITY IS:          663.8309      MILLIDARCIES

ENTER FINAL PRESSURE: 24.8

ENTER FLOWRATE:  12.6
THE PERMEABILITY IS:          2.43459       MILLIDARCIES

ENTER FINAL PRESSURE:  23.3
```

ENTER FLOWRATE: 220
THE PERMEABILITY IS: 51.62549 MILLIDARCIES

ENTER FINAL PRESSURE:

EXAMPLE FOR PROCESSING MINI-PERMEAMETER DATA

DEPTH	FLOW RATE	PRESSURE	ATMOS PR	Ka
15.5	285	24.89	14.62	55.55
15	340	24.75	14.62	67.42
14.5	316	24.72	14.62	62.90
14	235	24.93	14.62	45.58
13.5	273	24.78	14.62	53.94
13	269	24.77	14.62	53.21
12.5	165	24.95	14.62	31.93
12	304	24.60	14.62	61.43
11.5	45	25.32	14.62	8.33
11	100	25.01	14.62	19.21
10.5	163	24.83	14.62	32.01
10	230	24.64	14.62	46.24
9.5	279	25.54	14.62	50.32
9	75	24.88	14.62	14.64
8.5	41	25.10	14.62	7.79
8	62	25.06	14.62	11.84
7.5	216	24.53	14.62	44.03
7	200	24.39	14.62	41.50
6.5	72	24.94	14.62	13.95
6	155	25.54	14.62	27.95
5.5	81	24.81	14.62	15.94
5	146	24.50	14.62	29.88
4.5	283	24.19	14.62	60.26
4	460	23.83	14.62	102.73
3.5	121	24.42	14.62	25.01
3	59	24.71	14.62	11.76
2.5	154	24.37	14.62	32.04
2	85	24.55	14.62	17.28
1.5	125	24.49	I4.62	25.61
1	740	23.36	14.62	176.31
0.5	177	24.13	1.62	37.99

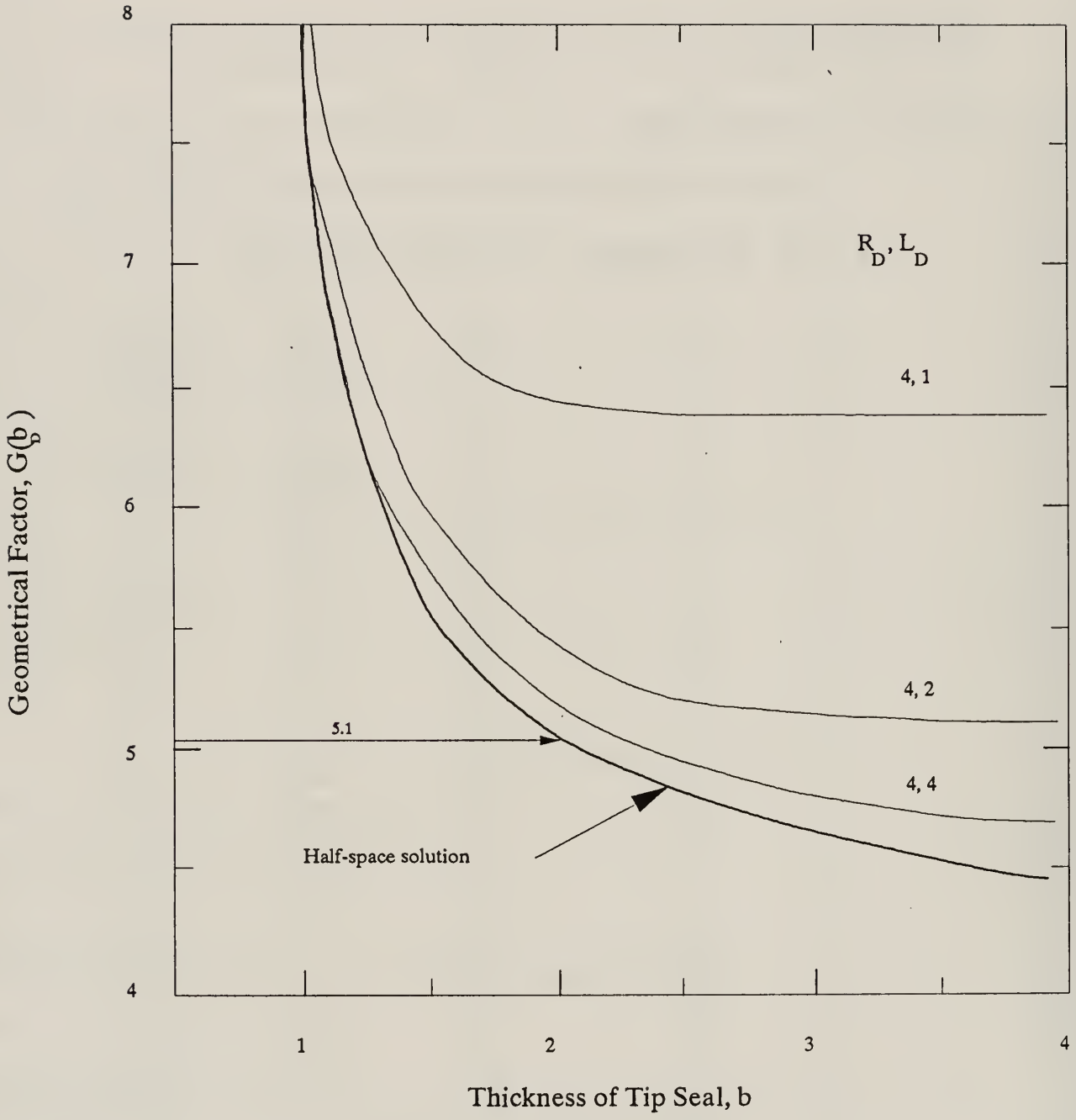


Figure 4. Determination of G_o

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Measure permeability at outcrop or on cores using a portable minipermeameter.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey or in the field.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Portable Permeametry	By field or project, e.g. Energy Field or MCA study	in publications	Various disks (Haggerty)	Engineering PCs

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

CORE FLOODING SYSTEM

Dennis J. Haggerty

Scope and Use of the Method

The Temco Core Flooding System is used to determine the liquid permeability of a core sample. The core flooding system consists of a Hassler-type core holder, two rodded cylinders, two clear cylinders, two Micromeritics fluid displacement pumps, an Enerpac hydraulic confining pressure pump, a differential pressure transducer, an 18 cubic-foot bench oven, corrosion-resistant connective steel tubing and valves, and various ancillary equipment. The accuracy of the method is primarily limited by the calibration of the differential pressure transducer. Air permeability values for the same samples are compared with the results for accuracy.

General Principles

A cylindrical plug cut from the core sample is inserted inside a rubber sleeve (one-inch I.D.) in the core holder. One-inch diameter end pieces (designed for radial flow) are interfaced with the plug inside the rubber sleeve. One-inch diameter spacers are used to fill any void space to accommodate plug lengths between one-fourth inch and twelve inches. O-rings (on end caps with retainers) seal confining fluid between the core holder casing and the rubber sleeve. The fluids to be injected (oil, brine, acid, etc.) into the sample are first brought into the system via the externally mounted clear cylinders. From there they are air-pressured into the rodded cylinders mounted inside the bench oven (behind the core holder). Each rodded cylinder contains a teflon piston which separates the injection fluid from the pumping fluid (typically distilled water). Valves on the front control panel facilitate the control necessary to load the desired fluid into either rodded cylinder. The Micromeritics displacement pump(s) (located above the valves on the control panel) is(are) purged and set to a predetermined flow rate. From here, the pumping fluid(water) flows through tubing to the top valve of the rodded cylinder forcing the teflon piston down and driving the injection fluid out the bottom of the rodded cylinder. Depending on how the valves are positioned, the flow continues through the plug (inside the core holder) in the selected direction. After the injection fluid passes through the plug, it flows (through corrosion resistant steel tubing) outside the oven through a back pressure regulator and out to the collection burette. Separate tubing lines interconnected at the inlet and outlet of the plug connect to opposite sides of the differential pressure transducer. The signal received from the transducer is displayed as per cent pressure drop (the diaphragm used here has a 100% deflection equal to 320 psig) on the front panel. A stable pressure drop value is used in Darcy's equation for isothermal, steady-state, linear flow to calculate liquid permeability.

Equipment and Apparatus

Two large cabinets (80" x 32" x 24" and 75" x 40" x 28") make up Temco's SSCF-3, 87-10-502 model Core Flooding System. One cabinet is a Despatch LDB 2-18BD forced convection airflow oven which houses the model number CRR-50-100-HB rodded cylinders, the model number RCHR 1742 core holder, and the corrosion resistant line valves. The other cabinet's components and attachments include: two model number 760 Micromeritic Displacement Pumps, model number BPR-05 Back Pressure Regulator, a Validyne DP303 Differential Pressure Transducer, an Enerpac model PER-2031 Hush-Pup hydraulic Pump, two Temco clear cylinders CC-10, Wika pressure gauges, and the valve control panel. Required equipment, not provided by the manufacturer, include a strong vacuum pump, nitrogen tank with a regulator, and an electrical supply.

Procedure (Figures 5 and 6)

1. Turn on the system by flipping the main power and auxiliary power toggle switches on the front control panel of the instrument and allow 20-30 minutes to warm up.

2. Load the core sample into the core holder (note 1).

3. Apply desired confining pressure to the core holder (note 2).

4. Load the injection fluid into the proper clear cylinder (CC) (note 3).

5. Transfer the injection fluid from the clear cylinder to the rodded cylinder (RDCYL) (note 4).

6. Purge the pumping system (note 5).

7. Set oven temperature and keep door closed when possible (note 6).

8. Set back pressure (note 7).

9. Set pumping rate and maximum pressure limit (note 8).

10. Close all valves except the rodded cylinder valves and the core inlet valve (valve 21, 22, 23 and 24 for oil; 25, 26, 27 and 28 for water).

11. Start pump with valve V8 open and transducer bleed screws cracked for purging.

12. Close bleed screws when gas-free fluid begins to seep out.

13. Close valve V8 and allow pressure to climb to the approximate pressure of the back pressure regulator.

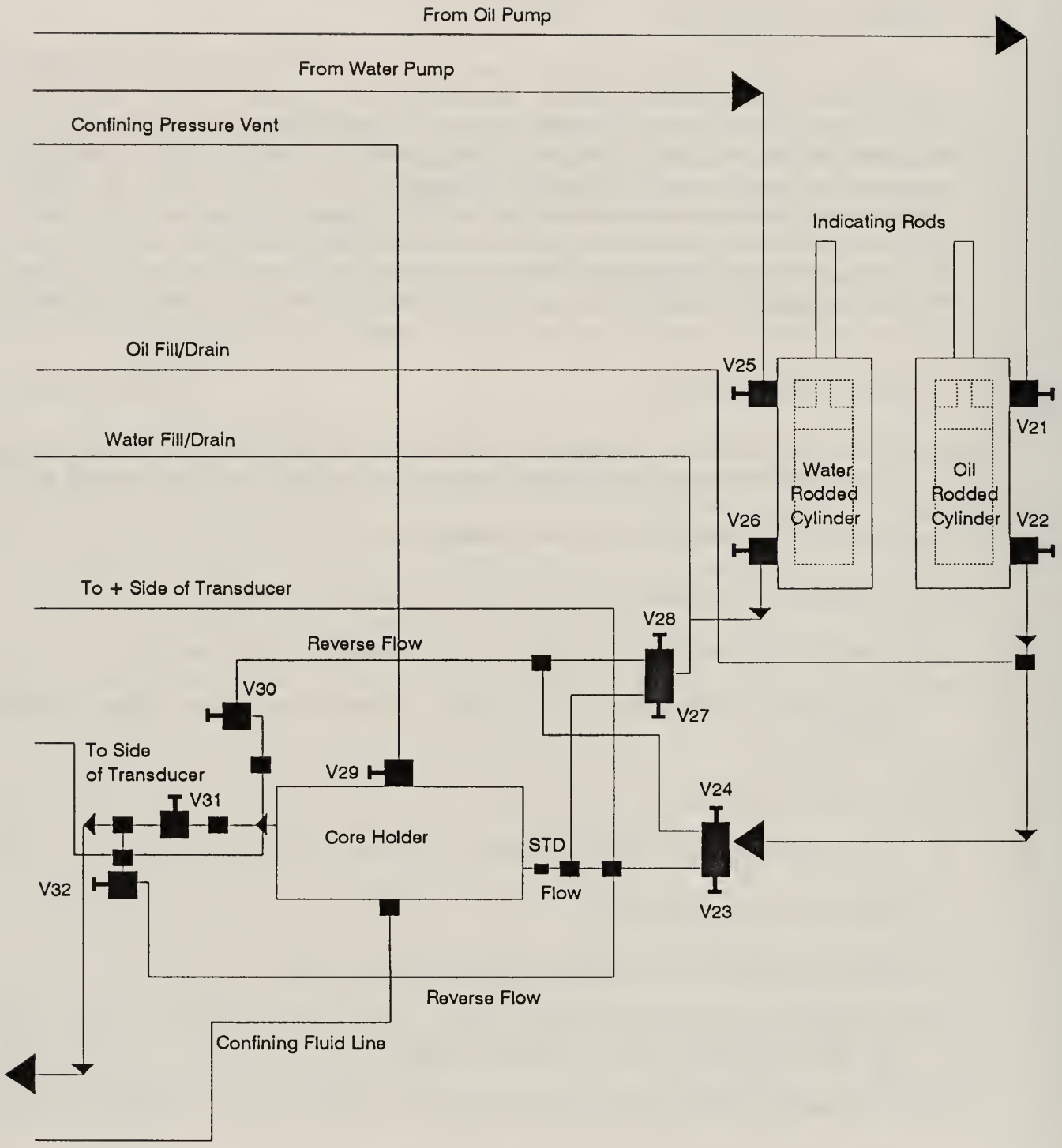


Figure 5. Oven Cabinet Flow Line Diagram

SOP-5

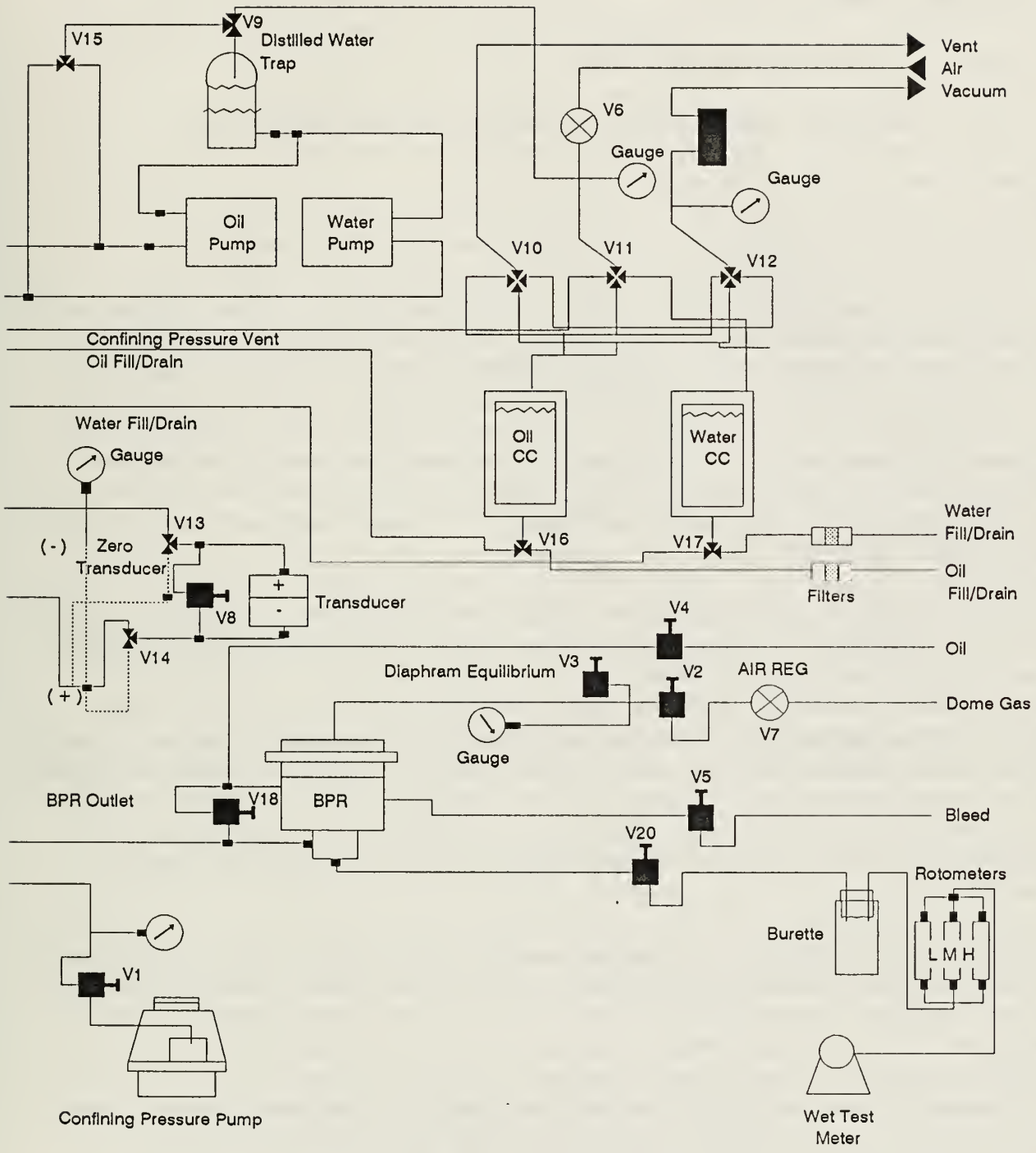


Figure 6. Control Panel Cabinet Flow Line Diagram

14. Slowly open valve V31 for standard flow (valve V30 and V32 for reverse flow) and let fluid flow through core plug.

15. Slowly open valve V18 and valve V20.

16. Monitor all gauges, check for leaks, and make any necessary adjustments.

17. Drain burette of effluent to avoid overflow.

18. Monitor injection fluid level in rodded cylinder and add when necessary.

Note 1: Core sample installation. Screw end caps into the core holder making sure O-rings are in good condition (apply a slight amount of vacuum grease). Slide the core sample through the ferrule and into the rubber sleeve. If the sample does not easily slide into the sleeve, a vacuum can be applied through the annulus pressure port by opening valve V29 and valve V12 (open to core). Install the distribution plug through the ferrule and against the core face on each end. Insert the necessary size spacer(s) making sure sample plug remains in the center of the core holder, and then screw in the retainers hand-tight. Reconnect the inlet and outlet tube fittings; if the proper spacers are used, no play will be observed in the flow lines.

Note 2: Applying Confining Pressure. Close valve V1, open valve V29, and turn valve V12 to the core position. Activate vacuum pump (which should be connected to external vacuum port) and run until gauge reads at least negative 25 inches of mercury for 10 minutes. Then close valve V29, open valve V1, and turn off pump. Flip up the pump power and manual return toggle switches, both located near the center of the control panel. Press the white pressure button (also of the control panel) intermittently until the confining pressure gauge reads the desired pressure. Close valve V1, and flip the manual return toggle switch down to release the line pressure to the pump. If the pressure goes up too high, lower it by slowly opening and then closing valve V1, dropping the pressure to the correct point.

Note 3: Loading the Injecting Fluid into the CC. The injection fluid is pulled into the external clear cylinders through ports located on the right side of the control cabinet, one each for the oil- and water-based fluid. Initially, all the valves in the system are closed except valve V8. The vacuum pump is activated and valve V12 is turned to the OIL CC position (WATER CC if transferring water) and valve V16 is turned to the FILL position (V17 for water). When the supply container is nearly empty or the clear cylinder is within an inch of being full, valve V16 is changed to the RDCYL position (V17 if water). The vacuum is left on until gas bubbles stop flowing. Valve V12 is turned to the upright position (closed).

Note 4: Transferring from the CC to the RDCYL. All valves are initially closed. The nitrogen tank valve is slowly opened and if no leaks are detected, 20 psig is set on the

outlet gauge of the regulator. Valve V6 (air regulator) is turned clockwise until 25 psig is read on the control panel air pressure gauge. Then valve V11 is turned to the OIL CC position (WATER CC if water is being transferred) and valve V16 or valve V17 is turned to the RDCYL position. Valve V9 is turned to the DRAIN RDCYL UTILITY position and valve V15 to either DRAIN OIL or WATER, depending on what is being transferred. The top of the rodded cylinder is then removed by rotating it counterclockwise, and the rodded cylinder is filled with distilled and degassed water. Valve V21 (V25 if water is the fluid) is opened and the top of the rodded cylinder is then replaced. Valve V22 on the bottom of the rodded cylinder is opened (V26 if water) to allow fluid entry. The pressured nitrogen forces the oil (water) out of the clear cylinder and into the rodded cylinder through the connecting tubing. An indicating rod rises as the fluid level inside the rodded cylinder increases. Valve V16 (V17 for water) is returned to the upright position before the fluid level reaches the bottom of the clear cylinder so that no air enters the system. Valves V9 and V15 are closed and the air (nitrogen) pressure is released by unscrewing valve V6 and opening Valve V10 to the OIL CC (or WATER CC) position for 30 seconds.

Note 5: Purge the Pumping System. The Micromeritics pumps are located on the middle shelf of the control center cabinet, number 1 for the oil-based system and number 2 for the water-based fluid system. The pumps are activated when the auxiliary power switch is flipped on (located on the front of the pump). A knurled vent valve, located on the front right of the pump, is opened and the red purge key held down; distilled water will begin surging out in drops. When no gas bubbles are observed, the vent valve is closed and the purge key is released.

Note 6: Setting Oven Temperature. To set the oven temperature, the power and heater switches are turned on and the temperature in degrees centigrade is dialed in on the digital indicator; this is done by pushing in the white button and turning the control knob until the number selected is displayed.

Note 7: Set Back Pressure. To set back pressure, the nitrogen gas source must be connected to the "Dome Gas" port situated on the right side of the control panel cabinet. Valves V2 an V3 are opened and nitrogen regulator is set to the required pressure. The dome gas regulator valve, V7, is turned clockwise until the dome gas gauge reads the correct pressure. Valves V2 and V3 are closed and the regulator valve is turned counterclockwise, releasing the excess gas. The nitrogen gas source is closed and detached.

Note 8: Set Pumping Rate and Maximum Pressure Limit. To set the pumping rate, the Micromeritics pump must be activated (see note 5.). Hold down the flow "set" key and the up or down arrow key at the same time (A digital display will show the flow rate setting in cubic centimeters per second). Release both keys when the correct value is reached. Setting the pressure maximum limit (for safety) is done by holding the pressure "max" key and the up or down arrow key in at the same time. The digital display will show the pressure in mega pascals (MPa). An Mpa is equal to approximately 145 psi.

Calculations

Darcy's equation for linear flow is used to calculate the liquid permeability of the core sample being tested. The equation

$$Q = k\,(A\Delta P)/(\mu L)$$

where: **Q** = volume flow rate, cc/sec
k = permeability, darcys
A = cross-sectional area, cm^2
μ = viscosity, centipoises
Δ**P** = pressure drop, atm
L = length, cm

is rearranged to: $k = Q\,(\mu L)/(A\Delta P)$

Example computation

Generated data:

Q - set at 3.50 cc/min
μ - by viscosimeter @ formation temp = 28.5 cp
A - from measured diameter = 2.54 cm in $A=\pi(d/2)^2 = 5.067\ cm^2$
L - from measurement = 5.024 cm
Δ**P** - from digital display = 10.4%

Note: Transducer diaphragm has 100% deflection = 320 psig

Adjust units: $k = Q/60sec/min\ (\mu L)/(A[320\{\Delta P/100\}])$

Or: $k(darcys) = 0.01667Q(\mu L)/(A[3.2\Delta P])$

Plugging in: $k = 0.01667(3.50)(28.5*5.024)/(5.067*[3.2*10.4])$

Results: **k** = 0.0506 darcys

or

k = 50.6 md (1 darcy = 1000 md)

Converting Cubic Centimeters per Minute(CC/MIN) To Feet Per Day(FPD)

3.60 cc/min * 60 min/hr * 24 hr/day = cc/day
5184 cc/day * $(1\ in.)^3/(2.54\ cm)^3$ * 1 ft/12 in. = 26.36 in^2ft/day

26.36 in^2ft/day ÷ cross-sectional area of core sample = ft/day
26.36 in^2ft/day ÷ [5.067 cm^2 * $(1 in.)^2/(2.54 cm)^2$] = 33.56 ft/day

Converting Feet Per Day(FPD) TO Cubic Centimeters Per Minute(CC/MIN)

1 ft/day * 1 day/24 hr * 1 hr/60 min = 0.0006944 ft/min
0.0006944 ft/min * 12 in/1 ft * 2.54 cm/in = 0.02117 cm/min
0.02117 cm/min * cross-sectional area of core sample = cc/min
0.02117 cm/min * 5.067 cm^2(1 in. diameter sample) = 0.11 cc/min★

Table 2. Conversion Table for One-Inch Diameter Core Samples

FPD	CC/MIN
1	0.11*
2	0.21
5	0.53
10	1.06
15	1.59
20	2.12
25	2.65
35	3.71
46.7	5.00 - maximum pump rate possible

★ - rounded-off to pump limit

Precision and Accuracy

The accuracy of the system is limited by the calibration of the differential pressure transducer within 0.5% of full scale. To minimize this effect, the diaphragm plate used in the transducer should not rate higher than twice the expected maximum pressure. The precision of the calculated millidarcys of permeability cannot be greater than the precision of any of the parameters in Darcy's Equation. In this case, three significant figures are possible provided the numbers used in the equation were not rounded off. Example: 4.21 md is credible, 12.34 md is not. 12.34 md should be presented as 12.3 md.

Other Parameters

Flow rate is preset on the Micromeritics pump in cc/min and can vary between 0.01 and 5.00. Core sample length and diameter are measured with a precision micrometer to the nearest 100th of a millimeter. The pressure is digitally displayed as per cent to the nearest tenth. Kinematic viscosity is determined with a Canon-Fenske Calibrated Viscosimeter. The resulting centistokes are multiplied by the pycnometer specific gravity to yield the dynamic viscosity in centipoise. The accuracy of the value for viscosity is within 1 per cent; and the precision is to the nearest 1000th of a centipoise.

```
C     PROGRAM PVKL
C
C     AUTHOR : HWI W.(WAYNE) BANG AND DENNIS J. HAGGERTY
C     DATE   : SEPTEMBER 1990
C
C     INSTRUMENT : INTEGRATED CORE FLOODING SYSTEM
C     EXPERIMENT : CORE FLOW TESTS
C                                  THIS PROGRAM COMPUTES ABSOLUTE AND
                                   EFFECTIVE
C                                  PERMEABILITIES AS A FUNCTION OF
                                   CUMULATIVE FRACTIONAL PORE
C                                  VOLUME INJECTED AND GENERATES OUTPUT
                                   DATA FILE FOR PLOT
C
C     INPUT REQUIRED IN USER SPECIFIED INPUT DATA FILE
C           Q     : INJECTION RATE (CC/MIN)
C           VISC  : INJECTION FLUID VISCOSITY (CP)
C           AL    : CORE LENGTH (CM)
C           A     : X-SECTIONAL AREA OF CORE (SQ. CM)
C           PV    : CORE PORE VOLUME
C           DPMAX : 100 % FULL SCALE OF DIAPHRAGM PLATE (PSID)
C           T(I)  : CUMULATIVE INJECTION TIME (MIN)
C           DP(I) : PRESSURE DROP (% OF FULL SCALE)
C     OUTPUT GENERATED IN USER SPECIFIED OUTPUT DATA FILE
C           CUMULATIVE FRACTIONAL PORE VOLUME INJECTED
C           VERSES LIQUID PERMEABILITY (MD)
C
      CHARACTER*30 ID,OD
      PARAMETER (NM=100)
      DIMENSION T(NM),PVINJ(NM),AK(NM),DP(NM)
      WRITE (6,20)
   20 FORMAT(1X,'ENTER INPUT DATA NAME : ')
      READ (5,40) ID
      OPEN (UNIT=50,FILE=ID,ERR=3000)
      WRITE (6,30)
   30 FORMAT(1X,'ENTER OUTPUT DATA NAME : ')
      READ (5,40) OD
      OPEN (UNIT=60,FILE=OD)
   40 FORMAT(A)
      READ (50,10,END=3000) Q,VISC,AL,A,PV,DPMAX
      DO 12 I=1,NM
      READ (50,10,END=3000) T(I),DP(I)
      IF (T(I) .EQ. 0. .OR. DP(I) .EQ. 0.) GO TO 11
   12 CONTINUE
```

```
   11  N=I-1
       QDPV=Q/PV
       QD60=Q/60.
       DO 13 I=1,N
       PVINJ(I)=QDPV*T(I)
       AK(I)=QD60*VISC*AL/A/(DP(I)*DPMAX/100./14.7)*1000.
       WRITE (60,14) PVINJ(I),AK(I)
   13  CONTINUE
   10  FORMAT(6F10.0)
   14  FORMAT(2F10.3)
 3000  STOP
       END
```

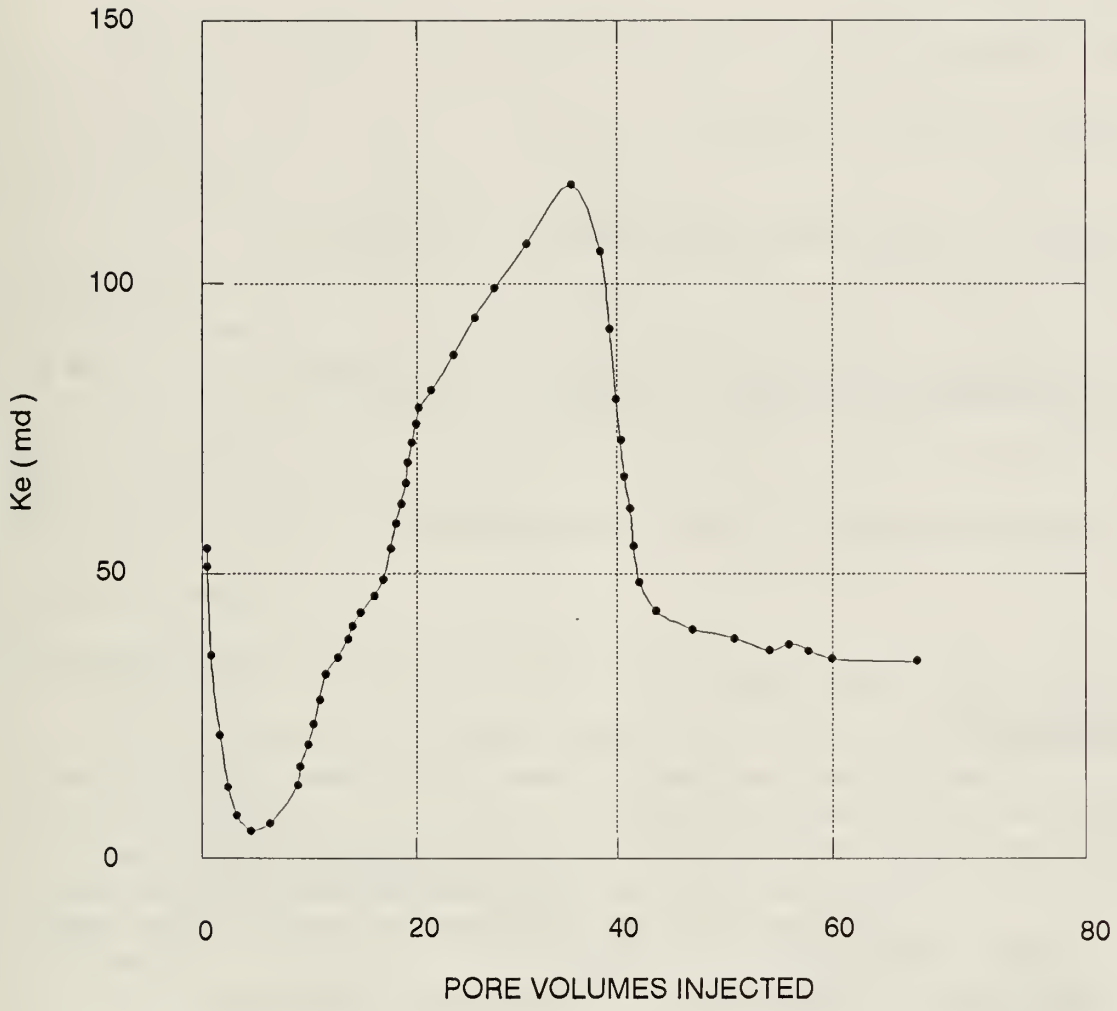
Input:

Q(cc/min)	μ(cp)	L(cm)	Area(cm^2)	P.V.(cc)	ΔP(max,psid)
time (min)	reading ($\%\Delta P$)				
"	"				
1.59	1.2908	3.992	4.8695	4.322	320
3.2	6.7				
4.33	8.4				
4.92	10.0				
7.27	18.4				
8.02	17.0				
8.37	16.4				
9.0	15.5				
10.45	12.7				
14.35	8.3				
15.25	7.4				
17.78	5.3				
19.03	4.7				
20.83	4.2				
22.53	3.8				
24.5	3.4				
25.5	3.3				
26.63	3.1				
27.2	3.0				
28.0	2.9				
28.25	2.8				
29.55	2.7				
30.93	2.6				
31.85	2.5 etc.				

Output:

Pore Vols. Injected .	Liquid Permeability(md)
1.177	19.227
1.593	15.336
1.810	12.882
2.675	7.001
2.950	7.578
3.079	7.855
3.311	8.311
3.844	10.143
5.279	15.520
5.610	17.408
6.541	24.305
7.001	27.408
7.663	30.671
8.288	33.900
9.013	37.888
9.381	39.036
9.797	41.554
10.006	42.940
10.301	44.420
10.393	46.007
10.871	47.711
11.379	49.546
11.717	51.527 etc.

See Figure 7 for an example plot.



Ke (md) vs. Pore Volumes Injected

Figure 7. Example Permeability Plot

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Determining liquid permeability of core samples.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Core Flow	By field or project, e.g. Energy Field or MCA study	in publications	Various disks (Haggerty)	Engineering PCs

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As needed.

CAPILLARY PRESSURE APPARATUS

Dennis J. Haggerty

Scope and Use of the Method

The Temco Capillary Pressure Apparatus is used to determine the bulk volume, pore volume and capillary pressure curve of a core sample of dimensions less than 3½ inches long and 1 1/8 inches in diameter. It follows the API specifications for the determination of bulk volume and porosity measurement by a technique referred to as liquid displacement mercury pump method. Mercury is used as the displacement fluid because of its chemical inertness and incompressibility characteristics. Mercury is pumped around a core sample enclosed in a calibrated steel pycnometer using a calibrated pump. The scale and dial arrangement allow easy reading of the volume of mercury displaced by the core sample. At zero psig the initial reading less the final reading is its bulk volume. Pressure is applied in incremental steps up to the point where mercury no longer invades any pore space in the sample. The increase in the pump volume reading is the pore volume, and divided by the bulk volume, equates to the porosity of the sample. The capillary pressure curve is the incremental pore volume readings versus the pressure applied.

Mercury Management

Warning:

Mercury is highly toxic and can emit vapors which can be readily absorbed through the skin. Rubber gloves should be used when handling mercury and open containers must have a layer of water covering the mercury at all times. Mercury will accumulate in the body and may cause central nervous system damage. If ingested, medical attention should be obtained; death from uremia is possible. If mercury poisoning is suspected, a urine specimen should be analyzed.

Chem Cycle, on the campus of the University of Illinois, will provide mercury at no charge. Their phone number is 244-7213. Otherwise, mercury can be ordered from AESAR/Johnson Matthey or other chemical company.

Quality:

The mercury should be free of any impurities. As the mercury is used, it should be continually inspected. If impurities are observed, they should be removed. Surface scum can be removed by pouring mercury through a glass bead column. Mercury-filled core samples should be sealed immediately after removal from the pycnometer chamber. Call 333-9278 and Hazardous Waste Management will pick them up.

Spills:

If the spill is widespread and involves over 50 cubic centimeters and is in an area of human occupancy, cordon off the area and request assistance from the Division of Environmental Health and Safety at 333-2755. If the spill is less than 50 cubic centimeters and confined, a vacuum flask partially-filled with water can be used to suck up the mercury until it can be recycled or disposed of properly. It is important to keep the mercury under water so that harmful vapors are avoided.

MP Series Mercury Capillary Pressure

Introduction

TEMCO offers a high pressure mercury capillary pressure apparatus for use in the measurement of bulk volume and porosity of core samples. Porosity, which is defined as the ratio of the void-space volume to the bulk volume of a material, is an intrinsic property of all reservoir rocks. The amount of void space which can be occupied by hydrocarbons and water within the reservoir must be known so that an accurate estimate of the petroleum or gas production can be estimated. The bulk volume of the sample must also be measured accurately to determine the correct porosity. TEMCO's mercury porosimeter and capillary pressure apparatus follow the API Specifications for the determination of bulk volume and porosity measurement by a technique referred to as liquid displacement and mercury pump method. Mercury is recommended as the displacement fluid because of its incompressibility and chemically inert character. Mercury is pumped around the core sample which is enclosed in a calibrated steel pycnometer. The pycnometer is an integral part of the pump. The pump is calibrated with a precision bore piston and a measuring scale. The scale and dial arrangement allow easy reading to 0.01 cc of total mercury volume and hence bulk volume and porosity. The volume of mercury displaced by the core sample represents the bulk volume of the sample. The porosity of the sample is then determined by a Boyle's Law type gas expansion and a mercury intrusion type test.

Equipment Description

1. Positive displacement pump, Model Number HAT-50-10

TEMCO's positive displacement pump is designed for the metering of fluids, measurement of volume and pressurization of systems. The design provides arms and plastic handles for easy operation. The pump has a calibrated piston for the precise metering and measurement of the displaced fluid. The linear and radial scales allow for easy measurement of displacement volume. The teflon packing gland seals the cylinder chamber and a special wiper is used to prevent damaging particles from entering the seal area.

2. Pycnometer

A pycnometer is mounted on the pump, making it an integral part of the pump. The pycnometer volume is precisely calibrated. The cap seats on an 0-ring and is locked in place by a quick-acting screw assembly. The internal void space is carefully designed so that upon the injection of mercury, no air is trapped around the core sample or within the pycnometer. The pycnometer is designed with two windows for measurement of the level of the mercury. The top of the pycnometer is connected to the Assembly Panel.

3. Assembly Panel

The Assembly panel comes with three absolute pressure gauges. The pressure ranges are 0-60 psia, 0-300 psia, and 0-3,000 psia. The panel is connected to the top of the pycnometer and the panel is also connected to a gas pressure source and a vacuum source.

Operating Procedure

1. Remove the pycnometer cap by turning the handles.

2. Advance the pump piston completely into the cylinder by turning the pump handles. The scale pointer should move to the 50 cc mark (or greater).

3. Pour approximately 25 cc of mercury into the pycnometer. Retract the pump piston from the cylinder by turning the handles until all of the mercury is in the pump cylinder. Advance the piston until the mercury starts to flow back into the pycnometer. Repeat this step until the pump cylinder is full. You are now ready to begin testing and calibration. (Note: The pump cylinder and parts to pycnometer and gauges will hold greater than 60 cc).

4. Screw the pycnometer cap assembly into place.

5. Open the valve on the assembly panel to the 0-60, 0-300, and 0-3,000 psia gauges.

6. Advance the pump piston into the cylinder until the mercury level is visible in the bottom window. Record the value of the volume on the pump. Now continue the mercury injection until the mercury reaches the level in the top window of the pycnometer. Record the value on the pump. The difference between the two numbers is the volume within the pycnometer. Repeat this procedure several times to verify the volume in the cell and to reproduce the results.

7. Repeat the procedure at various pressures up to the full rating of the pycnometer. Use the calculated values to determine the volume in the pycnometer at the various pressures. The volume will increase slightly with pressure as the metal expands.

8. Withdraw the piston until the sample chamber is empty.

9. Insert a sample core that has been extracted (i.e., all fluids removed) and dried.

10. Replace and lock the cap assembly and line up the mercury to the zero level in the lower window. Record the scale reading to 0.01 cc.

11. Advance the piston carefully until the mercury appears at the zero level in the upper window.

12. Record the scale reading to 0.01 cc. Calculate the bulk volume of the sample by subtracting this reading from the reading found in step 10.

13. Apply the pressure to the sample through the Assembly Panel and to the top of the pycnometer. Step the pressure in increments as desired. The initial pressures values could be 20, 50, 100, 200, 300, 500, 1,000, 1,500, 2,000 and 2,500 psia.

14. After the pressure is applied, the mercury will invade the sample. Turn the pump handle until the mercury level is again observed in the top window. Record the new value. The difference between the new value and the previous value is the amount of mercury that has invaded the core sample.

15. Repeat this procedure at each pressure stop. Record the data and analyze the data for bulk volume and mercury volume intrusion.

Pump Maintenance and Operation

Refer to Drawing Number B-1218 and Parts List Number P-1078 in the TEMCO Capillary Pressure Manual to identify the various components.

1. Chevron Seal Replacement

While awaiting the next pressure test, the teflon seals could have hardened and may no longer seal. Prior to any testing, the seals must be retightened. To tighten the seals, engage the provided pins into the holes on opposite sides of the seal ring retainer. Turn the pins in a clockwise fashion until tight by applying a combined torque of no more than 40 ft.-lbs. on the pins. Do not overtighten the pins because excessive torque could damage the holes.

If a leak persists, mercury will be observed in the bottom of the barrel. Drop the pressure in the pump cylinder and then attempt to re-tighten the seals. This procedure may need to be repeated several times to correct the problem.

The leak could be caused by a defective chevron seal. To replace a seal, drop the pressure in the pump and drain the pump of all mercury, being sure not to spill any mercury. Remove the pycnometer and gauges from the pump. Loosen the seal retainer. Retract the piston to the zero position. Unscrew the body from the pump support by turning counter-clockwise. Spanner wrenches may be required at this point. CAUTION: When removing the body, be careful not to scratch the piston. If the piston is scratched it will be necessary to replace the piston to insure a good seal.

After disassembly, inspect the piston, female adapter, packings, and male adapter for scratches or damage and repair or replace as required. In some cases an additional chevron packing may be required because the other packings have been deformed. Reassembe the pump in the reverse manner in which it was disassembled. As the female adapter is added, check to make sure that the adapter was inserted straight and parallel to the body.

After reassembly, tighten the seal retainer by applying a combined torque of 40 ft.-lbs. on the pins. Pressure the pump to 500 psi and then depressurize and re-tighten the seal retainer. Repeat this procedure in 500 psi increments to 2000 psi.

2. Lubrication

Lubricate the ACME screw thread with high pressure grease. Failure to lubricate the screw will cause additional wear on the screw. Without lubricant, additional torque will be required to operate the pump.

Recommended Spare Parts for Two-Year Operation

Part #	Quantity	Description
VS-1422	10 sets	Chevron packings
19-212	24	Pycnometer Seals

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Determine bulk and pore volume and capillary pressure on core samples.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Capillary Pressure	By field or project, e.g. Energy Field or MCA study	in publications	Various disks (Haggerty)	Engineering PCs

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary

CARBON DIOXIDE-SOLVENT CORE CLEANER

Dennis J. Haggerty

Scope and Use of the Method

The Carbon Dioxide-Solvent Core Plug Cleaner is a state-of-the-art machine used for cleaning crude oil, drilling mud liquids, and water from a single piece of whole core or a batch of core plug samples. The system is faster than soxhlet extraction, does not coke crude oil in the sample as does retorting, and uses the proven core cleaning method utilizing carbon dioxide saturated toluene. The cylindrical cleaning chamber is a pressure vessel 4.75 inches in diameter and 10 inches deep. The vessel is heated electrically with a two-kilowatt, 220 volt heater enclosed in an explosion proof housing. A thermocouple driven panel meter indicates the vessel temperature. The solvent is pumped from an on-board supply tank to the cleaning vessel with an electrically driven, high pressure, explosion-proof pump. A cyclone separator with a stainless steel-packed, water-cooled, after-cooler is provided to separate the carbon dioxide and the used hot solvent when the vessel is drained. The used toluene (solvent) drains into an explosion proof electric still where it is recovered and returned to the clean solvent supply. The still operation is automatic. The process controls are housed in a control box mounted outside of the hood. The solvent level is indicated on clear tubing outside the tank, and the dirty residue is drained from a separate tank through a valve located underneath the machine and properly discarded.

General Principles

Initially, carbon dioxide gas invades the sealed cylinder containing the unclean plugs to the pressure set on the carbon dioxide regulator (about 240 psi). Solvent is pumped into the carbon dioxide-charged vessel intermittently, until only one phase exists. After a suitable soak time the solvent is drained at a slow rate to prevent fracturing of the samples, and the process is repeated. Moderately permeable sandstone samples with light oils require only one "short" cleaning cycle; low permeability rocks with heavy crude oil present may require several "long" cleaning cycles. One "short" cycle lasts 3 hours, while one "long cycle" takes 12 hours. After the cycle is complete, the plugs are placed in an oven, to remove any residual solvent present. Our rule-of-thumb temperature setting as of this time (changes will be made as experience is accumulated) is to set the cleaning temperature at 50°F above the logged reservoir temperature (of the particular rocks being cleaned). Because this temperature is on the low side for maximum efficiency cleaning, we use a combination of solvents to enhance the cleaning process. Our efforts have determined that a mixture of two-parts toluene plus two-parts hexane plus one-part methanol works the best.

Equipment and Apparatus

The Carbon Dioxide-Solvent Core Cleaner is custom built by Harbert Engineering of Tulsa, Oklahoma. Necessary supplies not included by the manufacturer are the carbon dioxide tank with regulator, the solvents, a cooling water source and drain, 220 volt-35 amp/60 Hz electrical service, and an exhaust hood.

Procedure

1. Remove the cell lid by turning counterclockwise and lifting.
2. Remove the basket in the cell and place the samples to be cleaned inside the basket.
3. Gently lower the basket back into the cell and replace the lid by turning it clockwise until it becomes tight and locks.
4. Turn on the cold water tap and check the still outlet to adjust flow rate (moderate to fast without leakage).
5. Throw the breaker to the on position to connect the electricity source to the equipment (located directly behind the cleaner).
6. Flip the System On toggle switch located on the wall control box.
7. Turn on the fume hood.
8. Make sure make-up air is functioning properly.
9. Select the desired cycle (long versus short) by flipping the toggle switch also on the wall control box.
10. Set the temperature by pushing in the three-digit rolling dial to the desired degrees Fahrenheit.
11. Open the carbon dioxide tank and regulate a delivery pressure of 240 psi (with the present setup).
12. Begin the cycle by flipping to the Automatic Start position. (note: make sure the drain switch is in the open position)
13. Monitor the system for malfunction or leakage and in case of failure throw the breaker to off.
14. When the <Cycle is Complete> and <Drain Open> lights are the only ones on, and the temperature of the system is below 120°F, close the main valve on the carbon dioxide tank.
15. Flip the System On switch to the System Off position.
16. Turn off the cold water tap.
17. Throw the breaker box back to the off position.
18. Remove the lid and retrieve the cleaned plugs.
19. Turn off the fume hood.

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Dennis J. Haggerty

Objectives/Purposes: Clean oil, drilling mud and water from core plugs or whole core in preparation for experimentation.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Core Cleaning	NA	NA	NA	NA

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - NA

Changes - As necessary

PVT SYSTEM

Steve S.K. Sim

The phase behavior of a mixture of oil and gas during the production of a reservoir is very complex due to the number of components in the mixture. No reliable mathematical model exists which will describe the pressure-volume-temperature relationship of an oil and gas mixture with enough precision to be directly applied in petroleum reservoir or production engineering. Thus, laboratory PVT tests are still the most accurate way of obtaining the necessary thermodynamic and transport properties of reservoir fluids.

In general, a representative reservoir fluid sample is obtained at the earliest possible stage in the production life of a reservoir either through a direct bottom-hole sampling technique or by recombination of surface oil and gas samples. The sample is then transferred into a PVT cell in the laboratory and a series of reservoir fluid analyses are performed to determine the phase behavior of the mixture and the pressure-and temperature-dependent physical properties such as volume, viscosity, density, compressibility and solubility.

EQUIPMENT DESCRIPTION

The PVT equipment was designed and manufactured by D. B. Robinson Ltd. of Edmonton, Alberta, Canada. It consists of a recombination cell system, a PVT cell with capillary viscometer system, two Jefri manual positive displacement pumps and a motorized double-barrel opposed pump (fig. 8).

Recombination Cell System

The recombination cell system consists of a recombination cell mounted on a rocking mechanism and housed in a temperature controlled airbath. It is designed for recombining reservoir oil with solution gas to attain the original reservoir fluid composition, or a fluid mixture at a specified bubble point pressure. Bubble point determinations using the pressure volume method are accommodated by the presence of a sight glass mounted within the cell top cap. This allows direct, visual observation of the final bubble. A thermocouple port built into the cell body allows direct sample temperature measurement. The recombination cell contains a floating piston, which allows the use of mineral oil as the displacement fluid. The pressure of the mixture in the cell is measured with a Heise digital pressure transducer.

Jefri PVT Cell System

The PVT cell system consists of a Jefri PVT cell mounted on a rocking mechanism and housed inside a temperature controlled airbath. The PVT cell incorporates various features designed to enhance accuracy and to facilitate ease of operation. The fluids to

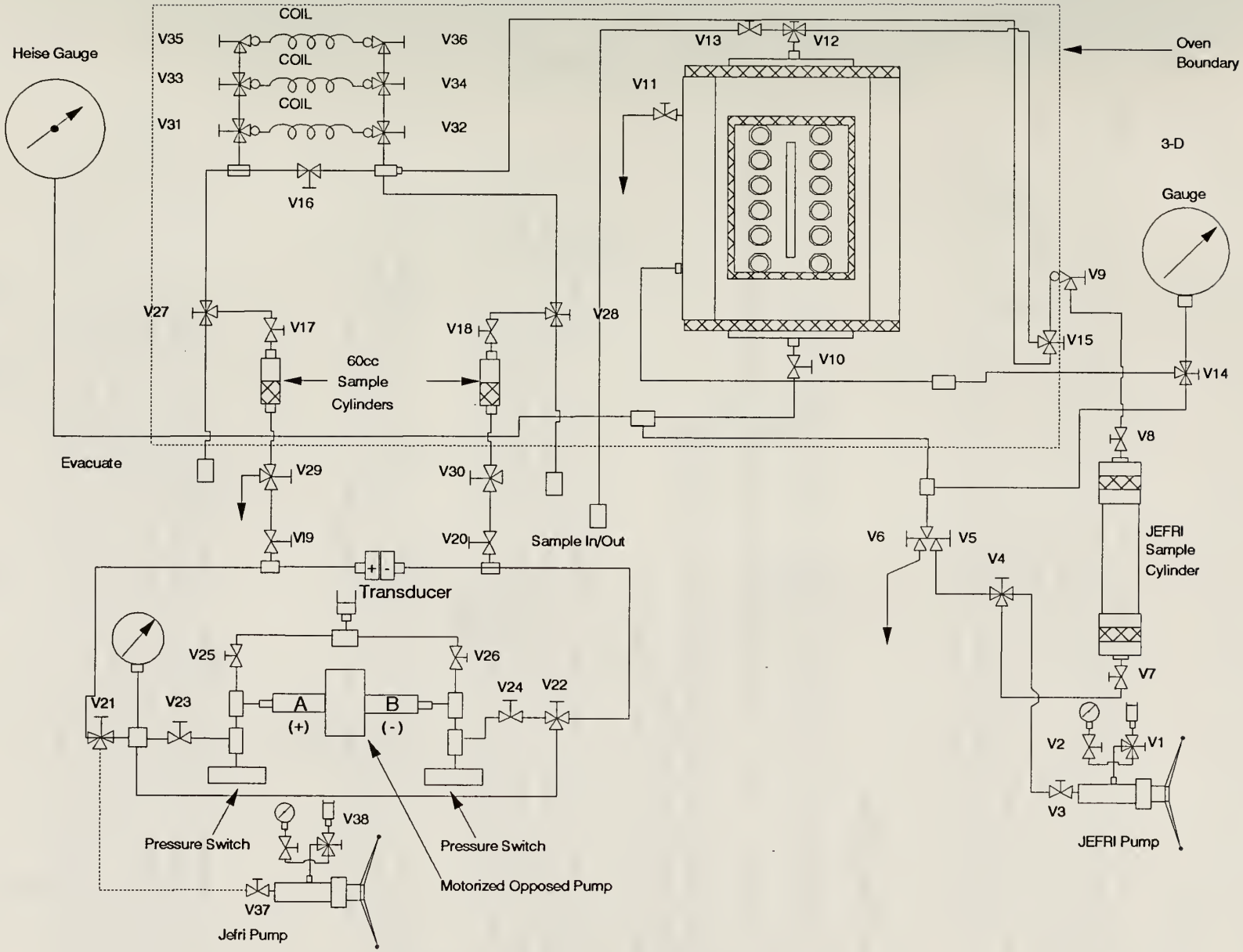


Figure 8: Schematic of Jefri Phase Behavior System with Viscometer
D. B. Robinson Design & Manufacturing Ltd

be studied are contained within a transparent glass cylinder which is secured between two full-length sight glass windows. The space surrounding the glass tube is filled with a transparent fluid, which is used to exert an overburden stress on the glass, equal and opposite to the pressure on the process fluid, thus visibility of the entire contents of the cell is unimpaired.

A further benefit of the glass sample cylinder - overburden pressure system, is that the sample volume remains dimensionally constant throughout the cell's total operating pressure range of 0 to 10,000 psi. This zero expansion necessitates only one volume calibration factor, and allows the use of a floating isolation piston. The isolation piston eliminates the requirement for mercury as the displacement fluid medium. This is preferred for occupational health reasons, and is necessary when laboratory studies are performed on fluids which contain compounds that are reactive with mercury, such as H_2S.

High Pressure Viscometer

The Jefri high pressure viscometer consists of four components:

1. A Jefri constant-volume, controlled-flow, high-pressure, double-barrel opposed pump.
2. Validyne differential pressure transducer and readout.
3. Uniform-temperature air bath.
4. Capillary tube with consistent geometry.

The high pressure fluid viscometer is designed to measure the viscosity of high-pressure, single-phase fluids. It operates on the principle that any fluid displaced in laminar flow through a capillary tubing of known dimensions exerts a pressure drop across the tube, which is related to the flow rate of the fluid passing through it. This relationship is a function of the fluid viscosity.

The Jefri motor-controlled opposed pump is a precision instrument which is capable of delivering high pressure fluids at very accurately controlled flow rates. This is achieved by combining stepping motor technology with modern precision machining procedures.

Jefri Gasometer

The Jefri gasometer (fig. 9) utilizes a motor-driven piston within a stationary cylinder. The displacement of the piston is monitored in order to determine the swept volume of the cylinder, and the pressure within the cylinder is automatically controlled at one atmosphere. As gas enters the gasometer, a pressure sensing device responds to any pressure change by instructing a motor to reposition the piston, thus restoring a null pressure reading within the gasometer. The movement of the piston is tracked by a

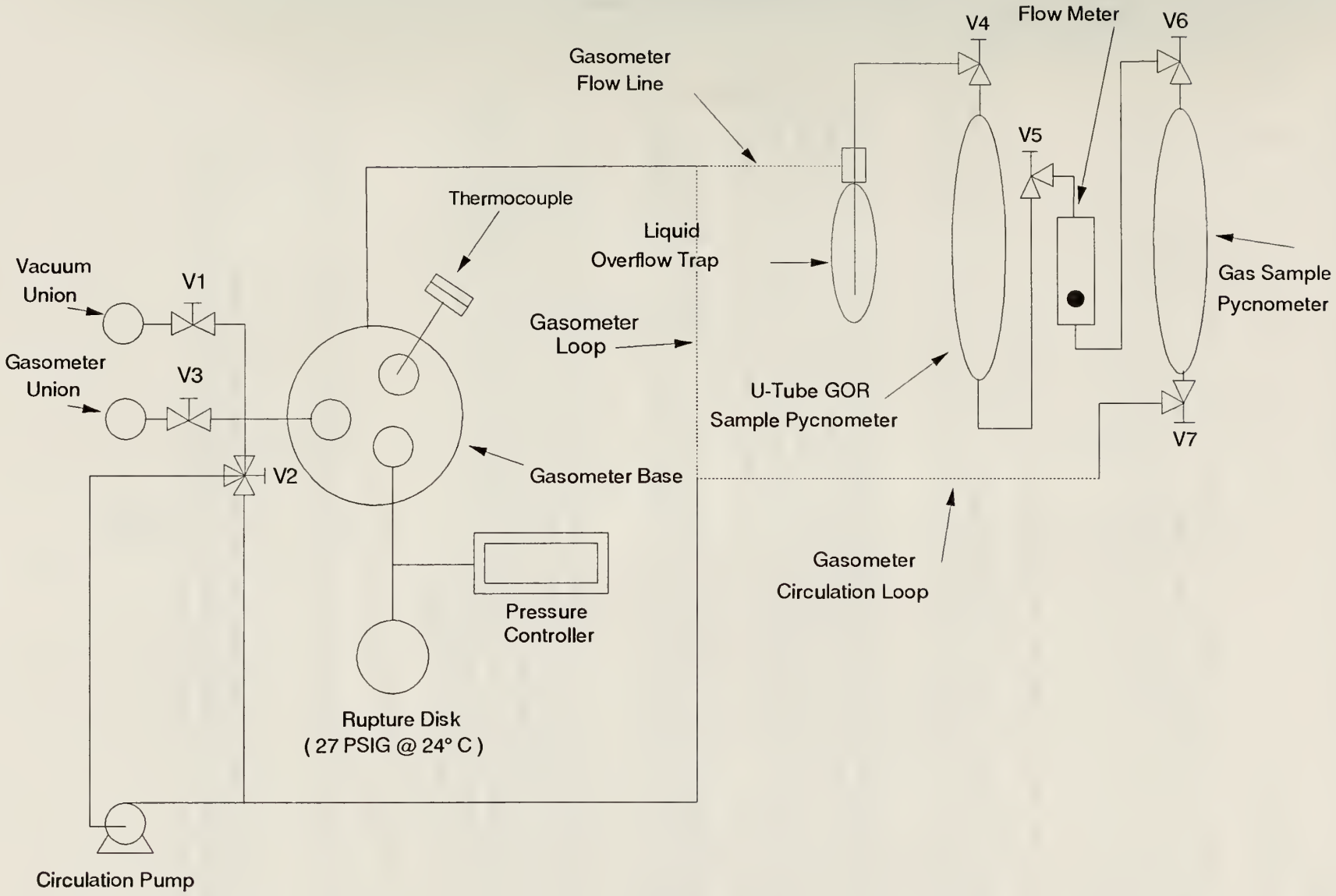


Figure 9. Jefri Gasometer/GOR Flow Schematic

linear encoder, the output of which is converted to indicate the volume of gas contained within the cylinder.

Experimental Procedures

The following procedures describe the operations without using mercury as the displacement fluid. The equipment may be converted to mercury operation by removing the isolation piston in the PVT cell, the recombination cell and the sampling cylinders. The advantage and limitations of operating without using mercury will be discussed in more detail below.

Recombination of oil and gas samples according to gas-to-oil ratio

1. Determine the volume of the recombined sample needed for the entire PVT study and then calculate the volume of solution gas and stock tank oil (or separator oil) needed for the recombination.

2. If the pressure of the solution gas sample obtained from the field is low, it can be increased by transferring into a smaller high-pressure cylinder (a special cylinder was prepared for this purpose) by cooling the smaller cylinder with liquid nitrogen. Care must be taken to make sure that the solution gas in the high-pressure cylinder is in a single phase. This can be achieved by heating the cylinder with heating tape.

3. The recombination system is set up as shown in Figure 10 with the cylinder containing the high-pressure solution gas sample connected to V4 via a three-way valve VE.

4. Evacuate the line via valve V3. Close valve V3, and open valve VA, V1, V2 V5 and introduce displacement fluid into the recombination cell until the piston reaches the top. (The pressure of the displacement fluid should not exceed 100 psi, as excessive pressure may press the piston against the top of the cylinder, thereby placing undue pressure differential on the piston seals; it will also require greater pressure to move the piston initially)

5. Evacuate the entire system through valve VE.

6. Close valve VE and open VD, to allow the gas sample to enter the recombination cell.

7. Withdraw displacement fluid from the recombination cell by means of the Jefri displacement pump (or through valve V3) until enough solution gas has been introduced into the recombination cell.

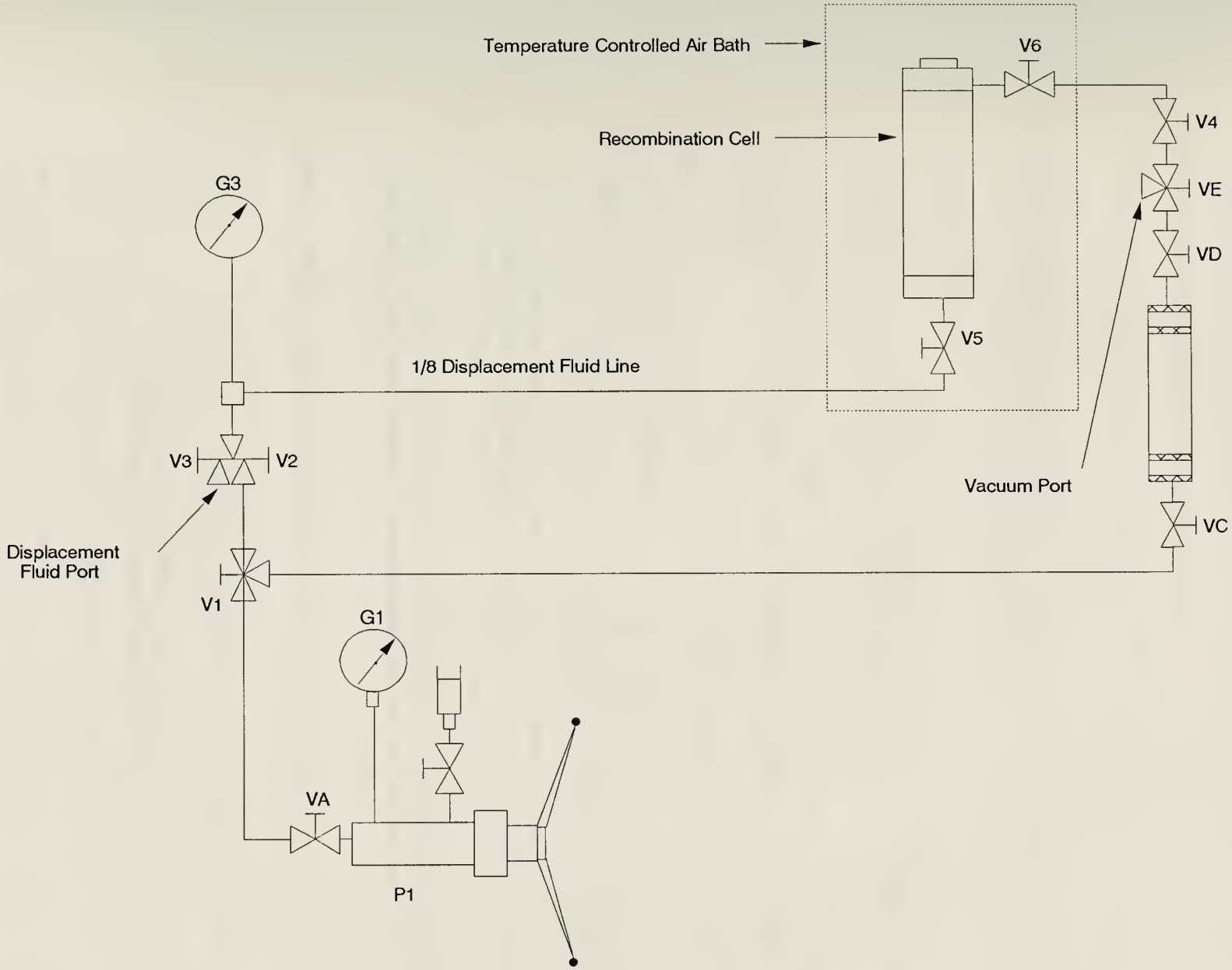


Figure 10. Schematic Layout of Charging and Discharging System

8. The amount of the gas sample within the recombination cell can be calculated from the pressure and volume of displacement fluid withdrawn from the cell, dead volume between valve V6 and the top of the piston (5.03cc), temperature, and the Z-factor of the solution gas.

9. The Z-factor of the solution gas can be calculated from the gravity of the solution gas, temperature and pressure.

10. If the composition of the solution gas is not available, direct measurement of the Z-factor of the gas can be made by expansion of a known volume of the gas from the recombination cell into the gasometer using the following formula.

$$\text{Gas expansion factor} = \frac{\text{Volume of gas at standard condition}}{\text{Volume of gas at reservoir condition}}$$

11. Calculate the volume of oil needed to obtain the specified gas-to-oil ratio.

12. Replace the gas sample cylinder with the oil sample cylinder.

13. Close valves V2 and V3 and open valves VA, V1 and VC.

14. Pressurize the oil sample to twice the pressure of the solution gas in the recombination cell or 1000 psi above the saturation pressure, whichever is higher (if the oil sample is a separator oil, ensure that it is in a single phase).

15. Evacuate the line between valves VD and V6, through VE, then close VE to the vacuum pump. Fill the line up to V6 with the oil sample while maintaining the pressure of the oil by injecting displacement fluid into the oil sample cylinder.

16. Take an initial volume reading of the pump, open V6 and inject the calculated volume of oil sample into the recombination cell. Take the final pump volume reading and pressure reading.

17. Close valves V6 and V4. Decrease the pressure in the oil sample cylinder to about 1000 psi above its saturation pressure.

18. Close valves VC and V1 and open valves V2 and V5.

19. Pressurize the recombination cell to a pressure about 1000 psi above the expected saturation pressure by injecting displacement fluid into the cell.

20. The rocking mechanism can now be activated and the pressure monitored.

21. Continue to inject displacement fluid into the cell to maintain the system pressure until the pressure stabilizes (when all the gas goes into solution).

Recombination according to saturation pressure

1. Follow the above procedure to step 12.

2. Take the initial pump volume reading, open valve V6 and introduce about 80 to 90 percent of the calculated amount of oil sample needed to obtained the required saturation pressure into the recombination cell.

3. Close valves V4, V6, V1 and VC.

4. Turn on the oven heater and the rocking mechanism and the content of the cell can be left to reach the temperature setting for the test.

5. Once the temperature is reached, displacement fluid can be displaced into the cell by opening valves VA, V2 and V5 using the pump, until the specified pressure is obtained.

6. By means of the window built into the top of the cell, and a flash light, determine if all the gas has been dissolved.

7. Additional oil sample can be introduced into the cell using the procedure described above until all of the gas just goes into solution at the specified pressure. Always maintain the pressure of the oil sample in the cylinder higher than the pressure of the recombination cell during the addition.

8. The pressure of the cell can then be increased to above the saturation pressure, and the heater of the oven can be turned off. During the cooling period, additional displacement fluid will have to be displaced into the cell to maintain the pressure above the saturation pressure.

Transfer of samples from recombination cell to sample cylinder

1. Knowing the total volume of displacement fluid injected into the recombination cell during the entire experiment, an appropriate volume of sample cylinder for sample transfer can be estimated. Prior to attaching the sample cylinder to valve VE, the sample cylinder must be filled completely with displacement fluid until the piston just touches the top of the cylinder. There should be little or no pressure under the piston. Evacuate lines from VD to V6 through VE and then close VE.

2. Sequentially open valves V6, V4 and VD to connect the entire system, maintaining the pressure within the system to that within the recombination cell, using pump P1.

3. The recombined sample is displaced from the recombination cell into the sample cylinder by injecting displacement fluid from P1 into the cell and bleeding displacement fluid from the sample cylinder by valve VC at a controlled rate.

4. Once the recombined sample is displaced, valves VC and VD are closed.

5. V4 is closed and VE is opened to vent the line, then the sample cylinder can be removed. Retract pump P1 to reduce pressure in recombination cell.

After the reservoir fluid has been prepared, the following reservoir fluid analyses can be performed.

a. Saturation pressure determination
b. Pressure versus volume study
c. Flash separation studies
d. Differential liberation studies
e. Oil viscosity versus pressure studies.

These tests are performed by means of the Jefri phase behavior system with viscometer as described below.

Priming the PVT cell with overburden fluid

Before the PVT cell can be considered operational, the overburden fluid must be primed. Otherwise the Pyrex sample containment cylinder may suffer damage.

The following describes the recommended procedure for charging the overburden fluid into the PVT cell (fig. 8, schematic of Jefri phase behavior system with viscometer).

1. Install an isolated piston into the PVT cell as described on Page 20 of the maufacturer's operating and maintenance manual for the Jefri high pressure PVT cell (D. B. Robinson Design and Manufacturing Ltd).

2. Open valve V10 and V14. Close all other valves.

3. Attach a vacuum pump to V11, open the valve and draw a vacuum on the overburden portion of the cell. Once the maximum attainable vacuum has been achieved, close V11.

4. Use V6 to admit the overburden fluid into the overburden cavity.

5. When the overburden cavity and volume under the isolation piston is completely primed, close V6 to contain the fluid.

6. Close V10, open V2, V3 and V5 and pressurize the overburden up to 200 psi (Warning: do not over-pressurize, the pyrex cylinder will not withstand a pressure difference of more than 500 psi), now close V14 to isolate the overburden pressure and then depressurize the pump. The cell is now ready for calibration or use.

Determination of sample volume in the PVT cell

When mercury is used as a displacement fluid, the volume of reservoir fluid in the PVT cell is determined indirectly from the pump reading corrected for the compressibility and thermal expansion of mercury. The accuracy of volumetric determination is limited by the readability of the pump (±0.01cc). Also, during operation at pressure below 500 psi, the accuracy will deteriorate a great deal due to expansion of gas bubbles trapped in the connecting lines.

To operate without using mercury, a floating piston is employed. The total volume of the sample confined in the PVT cell (between the inlet valve and the top of the piston) is measured by taking cathetometer readings of the position of the piston. No correction of displacement fluid compressibility and thermal expansion factors are necessary. The readability of the cathetometer is ±0.01 mm (corresponding to 0.008 cc of cell volume). However, the reproducibility of the cathetometer reading is subject to the following errors.

1. The cell body is not vertical after rocking.

2. Misalignment of the cross hair of the telescope with the reference point on the cell window or the isolation piston.

To minimize these errors, the following procedures are recommended.

1. Make sure that the PVT cell is vertical by checking the two index lines of the leveling devices attached to the cell rocking mechanism.

2. Check the horizontal bubble of the cathetometer as well as the bubble of the telescope.

3. Move the telescope to a selected piston marker (usually the top of the piston is chosen). If the piston top is obscured by the presence of dark oil, then the piston bottom or the border between the top metallic ring and the teflon ring can be used.

4. Focus at the selected point of the piston.

5. Move the telescope to align with the bottom of the cell window. Set the upper cathetometer reading to be 0.00. Move the telescope to align with the top of the PVT cell. It should read around 164.47 (if not, repeat steps 1 through 5).

6. Move the telescope to align with the selected point of the piston and take a reading. The corresponding volume can be calculated from the equation shown in Table 3.

7. It is recommended that once the focus is set, no readjustment should be made between readings of the reference point (bottom of the window) and the reading of the piston position.

8. Unnecessary change of the cell position should be avoided between readings. (That is, during measurement of compressibility of fluid in the single phase region, no rocking of the PVT cell is necessary.) Compressibility data which is comparable to literature values can be obtained with this procedure.

9. During isobaric operation, for example, when the sample is withdrawn from the cell at constant pressure, the displacement pump reading can be used to complement the cathetometer reading taking account the thermal expansion coefficient of the displacement fluid.

Calibration of PVT Cell (fig. 11)

Calibration of the PVT cell is performed by means of a Jefri positive displacement pump. The overburden pressure is set at approximately 200 psi and all valves are closed.

1. Open valves V2, V3, V5, V10, V12 and V9 (refer to fig. 8).

2. Fill the cell with 200 psi of nitrogen through V9 before connecting the Jefri sample cylinder. Move the piston level into the visible range within the PVT cell, (approximately 1-2 cm from the bottom of the milled window slot).

3. With a Jefri pump, inject displacement fluid in 10cc intervals, maintain constant pressure by venting through V9, then taking a cathetometer reading at each interval.

4. Calculate the volume to height ratio (.7931 as shown in Table 3).

5. Take a final reading of the piston near the top of the cell (with 200 psi pressure of nitrogen in the cell). Open V12 and V13 to vent the nitrogen.

6. Charge a Jefri sample cylinder with 70-100 cc of hexane.

7. Connect the Jefri sample cylinder through valve V9 (fig. 8).

8. Connect a vacuum pump to V13, and open it to draw a vacuum in the cell and lines (allow sufficient time), then close V12 and V13.

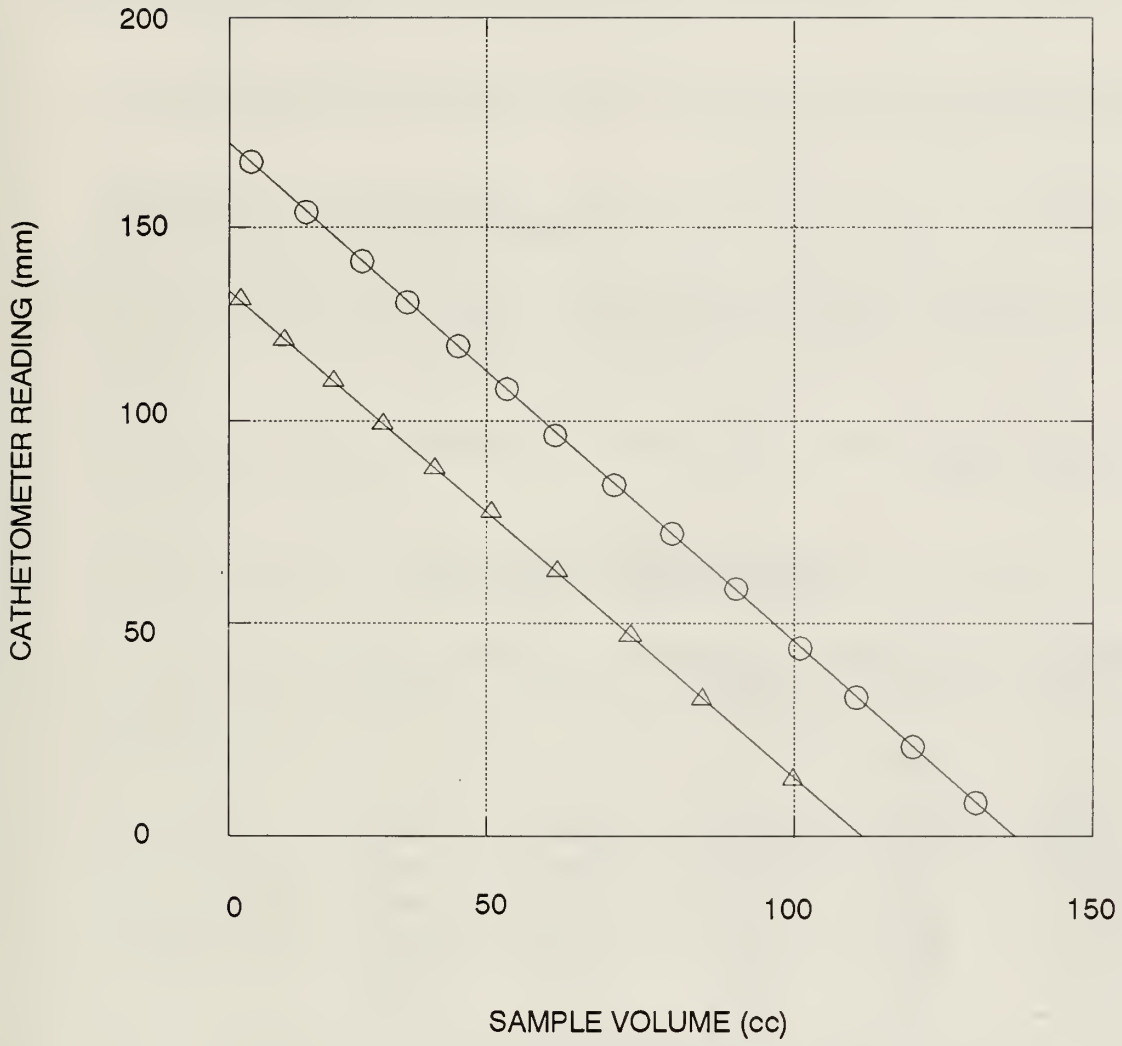


Figure 11. PVT Cell Volume Calibration

9. Open V4 and prime the tubing up to V7. Pressurize the hexane solvent to 200 psi. Open V8 and V9 and fill the line to V12, maintaining constant pressure on the Jefri sample cylinder at 200 psi, using the Jefri pump.

10. Take an initial pump reading, open V12 and inject hexane into the cell by throttling displacement fluid from the cell through V6, taking a final pump reading.

11. Displace solvent from the cell, evacuate the cell and repeat the total volume calibration to obtain an average value.

The calibration line is shown in Figure 11 and the calibration data are shown in Table 3. The maximum measurable volume is 131.62 cc when the top of the piston is visible near the bottom of the window. The minimum measurable volume of the cell is 1.14 cc when the piston is aligned with the top of the window. The average volume to height ratio is 0.7931 cc/mm giving an average area of the pyrex tube to be 7.931 cm^2.

When using piston cylinders to transfer liquid or gas samples, allowances should be made for the dead volume.

TABLE 3
Calibration of PVT cell volume

Pump (cc) (cc)	Difference (cc)	Cathetometer (mm)	Difference (mm)	Factor cc/mm
202.00	35.25			
212.00	10.00	47.73	12.48	0.8013
222.00	10.00	60.34	12.61	0.7930
232.00	10.00	72.95	12.61	0.7930
242.00	10.00	85.54	12.59	0.7943
252.00	10.00	98.14	12.60	0.7937
262.00	10.00	110.77	12.63	0.7918
272.00	10.00	123.38	12.61	0.7930

Average volume/height ratio = 0.7931 cc/mm

Sample volume = (164.47 - reading of piston top) x 0.7931 + 1.14

Sample volume = (135.39 - reading of piston bottom) x 0.7931 + 1.14

Transfer of reservoir fluid sample to the PVT cell

1. Clean and evacuate the PVT cell, bring the piston to near the top of the cell.

2. Attach the sample cylinder containing the reservoir fluid sample to valve V9 as shown in Figure 8.

3. With valves V13, V7, V8, V17, V18 and V28 closed, and V9, V15 and V16 opened, evacuate the PVT cell and the connecting lines.

4. Close valve V5. Open valve V4 and V3. Increase the pressure of the displacement fluid to at least 1000 psi higher than the saturation pressure of the sample.

5. Open valve V7 and adjust the pump pressure to about 1000 psi above the saturation pressure of the sample.

6. Close valves V15, V12 and V9. Sequentially open valves V8 and V9 to connect the entire system, maintaining the pressure within the system to that of the sample cylinder.

7. Take initial reading of the pump, throttle valve V12 maintaining the pressure of the sample cylinder.

8. When the top of the cell is filled with sample, and the cell pressure is approaching the pressure of the sample cylinder, valve V12 can be opened wide.

9. A predetermined quantity of sample can then be displaced into the PVT cell by injecting displacement fluid into the sample cylinder while bleeding displacement fluid from the PVT cell from valve V6 at a controlled rate.

10. Generally, between 50 to 100 cc of sample is required for the combined test of single stage flash separation and pressure volume relationship. A separate 60 to 90 cc of sample is needed for differential liberation studies. A third sample with minimum volume of about 100 cc is needed for the viscosity versus pressure studies.

11. After enough sample has been transferred, close valve V12, V8, V7. Open V13 to bleed the line pressure.

Determination of Thermal expansion coefficient of the reservoir fluid

1. Pressurize the sample in the cell to 5000 psi by injecting displacement fluid into the cell.

2. Rock the contents of the cell to ensure that it is in a single phase.

3. Align the cell in the vertical position, set up the cathetometer according to the procedure stated in the previous section, and take the cathetometer reading of the piston position as well as the cell temperature.

4. Lower the cell pressure to about 1000 psi above the saturation pressure, then the oven temperature control can be turned on to bring the sample to reservoir temperature.

5. Monitor the cell pressure constantly and adjust as necessary by withdrawing displacement fluid from the cell.

6. When the cell temperature has reached the desired setting, the cell pressure is increased to 5000 psi, and a final cathetometer reading can be taken. The thermal expansion coefficient can be calculated from the following formula.

$$\text{Thermal Expansion Coef.} = \frac{\text{Increase in volume}}{(\text{Oil volume}) \times (\text{Increase in temp.})}$$

Determination of the bubble point pressure at reservoir temperature

Starting from about 5000 psi, the bubble point pressure as well as the oil compressibility can be determined by the following procedure.

1. Withdraw the displacement fluid in small even increments, each sufficient to drop pressure approximately 1000 psi. Record pressure, pump reading and cathetometer reading after each withdrawal.

2. Repeat until within 500 psi of saturation pressure. Thereafter, take smaller displacement fluid withdrawals, approximately 100 psi drop per increment.

3. Agitate the sample by rocking the cell in a horizontal position. Visually check from time to time for the appearance of gas bubbles.

4. When the saturation pressure is reached, gas will come out of solution, tending to maintain pressure, causing a much smaller pressure drop per increment of displacement fluid withdrawal. Thorough agitation here becomes even more important. Thereafter, withdraw increments sufficient to cause 5 to 10 psi pressure drop until 50 psi below saturation pressure.

5. Take 20 to 25 psi increments thereafter until 150 to 200 psi below saturation pressure. Plot pressure versus pump readings on large scale, with best straight line through points above apparent saturation pressure. The break in the curve gives the saturation pressure.

Determination of relative volume versus pressure

Calculate the total sample volume from the cathetometer reading at each pressure. Divide the sample volume by the oil volume at saturation pressure. Plot the relative oil volume against pressure.

Single Stage Flash separation

1. Recompress the reservoir fluid sample to a single phase condition by injection of displacement fluid and agitation.

2. Prepare the 75 cc U-tube sample pycnometer (see fig. 9) by cleaning and evacuation.

3. Determine the tare weight of the sampler (806.4 g).

4. Set up the system according to Figure 8, but without the Jefri sample cylinder.

5. Connect the U-tube sample pycnometer to Valve V9 via a three-way valve.

6. Evacuate the line by means of the three-way valve, then close the valve.

7. Close valve V13; open V9.

8. Fill the transfer line from the PVT cell to the U-tube sampler, by throttling V12, maintaining the sample pressure by injecting displacement fluid into the cell. Open V12 completely when the line is filled. Adjust the sample pressure to the specified pressure.

9. Take an initial cathetometer reading of the position of the piston (a pump reading may be taken to complement the cathetometer reading).

10. Displace about 30 cc of sample into the U-tube sample pycnometer by throttling its inlet valve V4.

11. At the end of the displacement, close the inlet valve V4 of the sample pycnometer, adjust the pressure of the PVT cell before taking the final cathetometer reading and the pump reading.

12. Calculate the volume displaced from the cathetometer reading as well as the pump reading.

13. Determine the weight of the filled U-tube sample pycnometer. The difference between the filled sample pycnometer and its tare weight is the weight of the sample displaced.

Determination of the saturated oil density, GOR and formation-volume factor

1. The density of the sample at the system pressure and temperature of the PVT cell is:

   Weight of sample displaced/volume of sample displaced

2. Determine the tare weight of the liquid trap (96.15 g without teflon line, 125.46 g with line), gas sampler(650.90 g), calibrated volume of the gas sampler(71.12 cc), calibrated volume of the U-tube pycnometer (76.33 cc) and the dead volume of the gasometer (111.67 cc).

3. The U-tube sampler and the gas sampler are connected according to the flow scheme in Figure 9.

4. Using the downward control switch in the front panel, lower the gasometer piston until the lower travel limit is tripped. Take the initial reading of the digital counter mounted on the front panel.

5. Connect a vacuum pump to the vacuum union located on the front panel.

6. Once the maximum vacuum is drawn on the gasometer/GOR system, close vacuum/vent valve V1.

7. With the gasometer in manual mode, slowly and carefully open valve V4 on the tared GOR sample pycnometer to release the sample gas into the evacuated gasometer/GOR system. The flow rate for releasing the gas is metered using the pressure controller indicator. The plumbing includes a rupture disc which will burst if a pressure of 45 psig is exceeded during gas expansion.

8. When a positive pressure is reached within the system, the piston is raised manually to stabilize the system pressure to near atmospheric.

9. Maintain a positive system pressure while expanding the sample until the sample is completely flushed.

10. Expansion of the sample is continued until valve V4 is wide open and the pressure controller indicates atmospheric pressure.

11. At this point, the GOR sample pycnometer is released from its clamp and lightly agitated to release any latent gas from the remaining liquid. Monitor the gasometer/GOR pressure by controlling the gasometer displacement during this procedure.

12. As the gas production rate declines to zero, the GOR sample pycnometer is remounted and then the solution gas is released from the pycnometer. A two phase sample is prepared for equilibration by circulating the produced gas volume through the remaining oil.

13. Close the evacuate/circulate valve (V2) to connect the circulation loop, and push the circulation pump START button to activate the circulation diaphragm pump.

14. To initiate circulation, slowly open valve (V5) to percolate the produced gas through the remaining oil sitting in the bottom of the GOR sample pycnometer.

15. The circulation rate is controlled between 60-80 on the flow indicator by throttling through valve (V4) and adjusting the pump circulation rate.

16. Allow the system to circulate until the pressure stabilizes to atmospheric.

17. Close all the valves. Take the final reading of the digital counter. Remove the pycnometer from the clamp and measure its weight.

18. Determine the dead oil density by the conventional pycnometer method.

19. The volume of dead oil in the pycnometer is calculated from its weight and the dead oil density.

20. The volume of gas released is calculated from the following formulae:

    Gas volume = Difference in gasometer reading + dead volume + volume of gas sampler + volume of U-tube pycnometer - dead oil volume.

    Gas volume = difference in gasometer reading +111.67 +71.12 +76.33-dead oil volume.

The gas volume is then corrected to standard condition with the following equation:

$$V_1 = \frac{Z_2 P_2 V_2 T_1}{P_1 T_2}$$

where:

Z_2 = compressibility factor at system condition
P_2 = system pressure (psi)
T_2 = system temperature (degree Rankin)
V_2 = volume of gas at system pressure and temperature
V_1 = volume of gas at standard condition
T_1 = standard temperature (520 R)
P_1 = standard pressure (14.7 psia)

The gas-to-oil ratio is calculated as:

Volume of gas at standard conditions/Volume of dead oil at standard conditions.

The formation-volume factor is calculated as:

Volume of reservoir fluid at reservoir conditions/volume of dead oil at standard conditions.

Differential Liberation Test

1. Clean, evacuate and bring the piston of the PVT cell near the top of the cell (see fig. 8)

2. Charge the cell with 50 to 100 cc of sample using the procedure described under the title: "Transfer of reservoir fluid sample to the PVT cell."

3. Close valve V12, clean the line connecting valve V9 to V13 by flushing with toluene or hexane and dry with air.

4. Bring the cell temperature to reservoir temperature. Monitor the cell pressure and adjust accordingly.

5. Connect V9 to the gasometer union (fig. 9) through a liquid trap.

6. Bring the piston of the gasometer to the bottom, and evacuate the system including the connecting line. Then close the evacuation valve (fig. 9) and set the GOR meter mounted on the panel into auto mode.

7. Determine bubble point pressure of the sample in the PVT cell as done on page 81.

8. Withdraw displacement fluid from the PVT cell to drop the pressure 200 psi below saturation pressure. Agitate vigorously. Set PVT cell vertical, read pressure, read cathetometer and allow to sit five minutes. Open valve V12 slightly, displace gas at exactly constant pressure with the Jefri pump. Close valve V12 when oil sample reaches top of cell. Take cathetometer reading again.

9. Take the reading of the digital counter gasometer to determine the volume of gas released. Replace the gas sampler and evacuate the gasometer system and connecting line. Retain the gas sampler for gas analysis. If condensate is retained in the oil trap, it should be removed and weighed to determine the amount of condensate recovered.

10. Repeat steps 7 and 8 until the pressure is approximately 100 psig.

11. Perform a single stage flash separation of the remaining crude oil, as described above.

12. Calculate Bo, Rs, Bg and the oil density at each pressure point during the study. A program named DIFLIB.FOR, based on the principle of mass conservation, has been written in Fortran for the calculation. The input data needed for the calculation are: the reservoir temperature, volume of residual oil, density of saturated oil, density of residual oil, and saturation pressure. For each pressure point, the system pressure, the volume of gas at reservoir condition and at standard condition, gas gravity or gas composition, volume of saturated oil at reservoir condition are needed. A listing of the input data format is also included at the end of this section.

Measurement of the viscosity of an oil sample

1. Prepare the saturated sample in the PVT cell or with the recombination cell, using the procedure outlined under "recombination of oil and gas samples."

2. Close valves V21, V25, V26, V29, V30 and V15 (fig. 8).

3. Open valves V17, V18, V16, V19, V20, V22, V23, V24 and V27. Evacuate the double barrel pump and the 60 cc sample cylinders through valve V27 until good vacuum is obtained (minimum 0.5 hour).

4. With mercury or degassed distilled water in the reservoir, allow the fluid to fill the line between the reservoir and valves V25 and V26 by opening and closing valves V25 and V26.

5. Allow two minutes for the vacuum pump to remove the air introduced from the line.

6. Close valves V17, V18 and V27 and then shut off the pump. Open valves V25 and V26 slowly to allow the fluid in the reservoir to fill the pump and viscosity system. Do not allow the reservoir to run dry.

7. When the system is filled, close valves V25 and V26. The fluid pressure can be increased by means of an auxiliary 10cc positive displacement pump or by the following procedure.

8. With valves V22 and V25 open, close valve V24, start the motorized opposed pump toward the positive direction. Increase the system pressure to approximately double the required pressure. Stop the pump. Close valve V26, open V24, the negative side of the pump will be pressurized at the expense of the pressure of the system.

9. Introduce sample into the sixty cc sample cylinder on the right hand side. Evacuate all the connecting lines and the capillary tubing through valve V27 by opening valves V18, V31, V32, V33, V34, V35, V36 (and V15 if sample is introduced from the PVT cell) and closing V17, V18, V9 and V28.

10. Close the corresponding valves of the capillary tubing which will not be used. Increase the sample pressure to at least 1000 psi above its bubble point pressure.

11. Transfer the sample up to valve V28, purge sample, if necessary, to ensure single phase mixture.

12. Close valve V27, open valve V28 (or valve V15 if sample is from PVT cell) while maintaining the fluid pressure by injecting mineral oil into the sample cylinder or into the PVT cell.

13. Introduce between 5 and 10 cc of sample into cylinder B by opening valve V18, then slowly opening valve 30 to allow mercury or distilled water to drain out while injecting mineral oil into the sample cylinder (or the PVT cell) to maintain the sample pressure.

14. Close valve V30 when enough sample is introduced as indicated by the positively displaced pump reading.

15. Introduce between 20 to 30 cc of sample to cylinder A by first opening valve V17 and then valve V29.

16. Maintain sample pressure by injecting mineral oil into the sampling cylinder (or the PVT cell). Close valve V29 when enough sample is introduced.

17. Adjust system pressure with the positive displacement pump. Close valve V28 and V15.

The system is ready for viscosity measurement.

1. Select the pump rate, close valve V22 before opening valve V18, (Note, do not open valve V17, V18 and V22 at the same time since the fluid level in the 60 cc sample cylinder will try to equilibrate and it will cause a problem in sample volume tracking).

2. Turn the motorized opposed pump on (fig. 8) and then close bypass valve V16. Allow the transducer reading to stabilize (one-half minute) before taking reading.

3. Four to five rates of displacement are recommended. It is recommended to start at the highest rate and decrease at regular intervals.

4. The pressure drop normally stabilizes after one minute.

5. It is recommended that a strip chart recorder be installed to provide a smooth record of the pressure drop reading.

   Calibration of the three capillary coils was performed with both hexane and methane.

6. The 10 foot capillary tube (0.01 inch diameter) was calibrated with hexane. Eight flow rates were used ranging from 20 cc/hr to 200 cc/hr. The plot of pressure drop against flow rate gave a slope of 0.223 (psi-hr/cc). The viscosity of hexane at the condition of the calibration run is 0.289 centipoise. The capillary tube constant is calculated as 0.289/0.223 = 1.296 (Cp-cc/psi-hr) (fig. 12).

7. Similarly, the capillary tube with 0.01 inch diameter and 5 foot length was calibrated with hexane and has a tube constant = 2.55 (Cp-hr/psi-cc) (fig. 13).

8. The capillary tube with 0.005 inch diameter and 20 foot in length was calibrated with hexane.

   The capillary tube constant obtained using hexane as a standard is: 0.0293 (Cp-hr/psi-cc) (fig. 14).

9. A test run of the viscosity of the hexane saturated with methane at a saturation pressure of 650 psi was performed to investigate the effect of gas dissolution in water on the measured viscosity.

10. The result is shown in Figure 15. The viscosity is calculated as 0.205 centipoise.

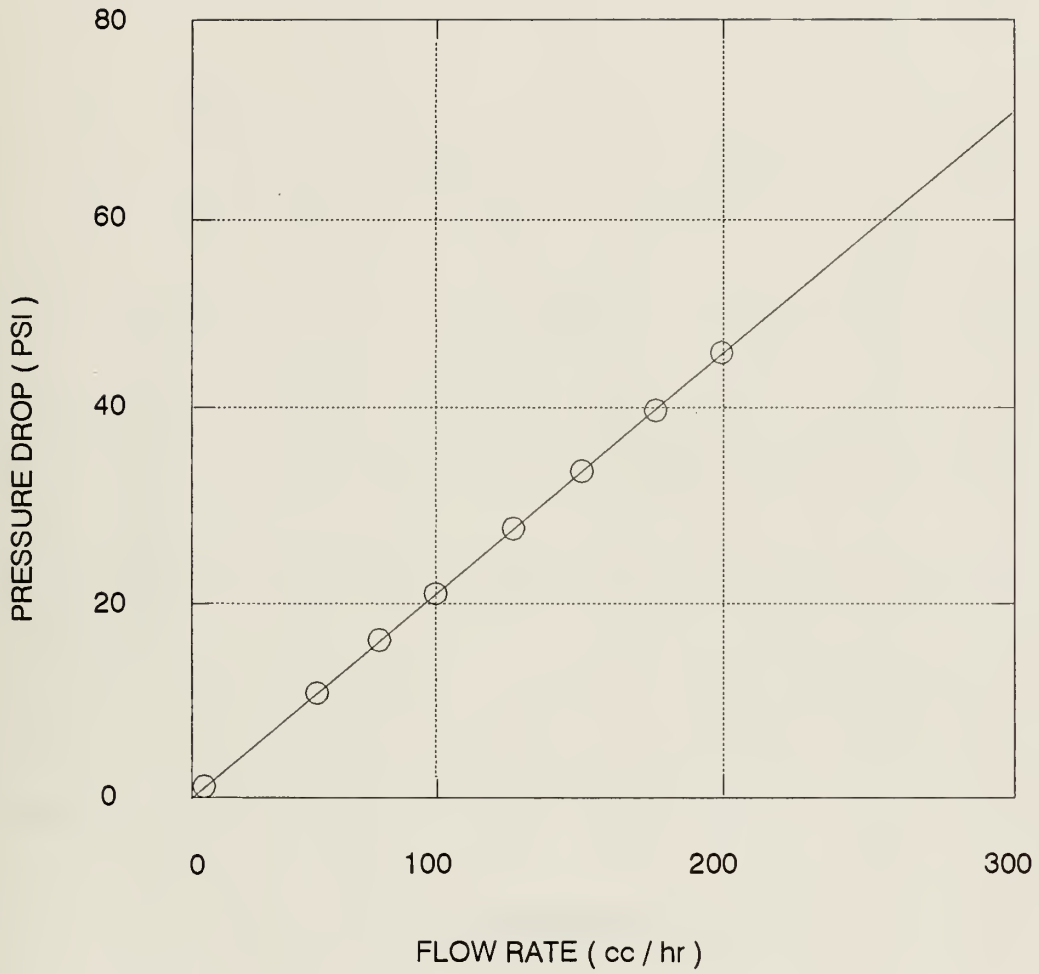
11. During the run, distilled water was used as the confining fluid. In order to minimize the change in composition of the sample due to dissolution of methane in water during the measurement, the contact time of the sample with water was kept at a minimum. Generally, four to five minutes was allowed for each pressure point with no more than half an hour for the entire viscosity measurement.

12. A second run was performed using hexane saturated with methane at a saturation pressure of 345 psig. The viscosity measured was 0.247 cp. (fig. 16).

13. The viscosity-composition plot of the hexane-methane mixture shows an expected trend of decrease in liquid viscosity with an increase in dissolved gas (fig. 17).

Fortran Source Code for DEFLIB.FOR

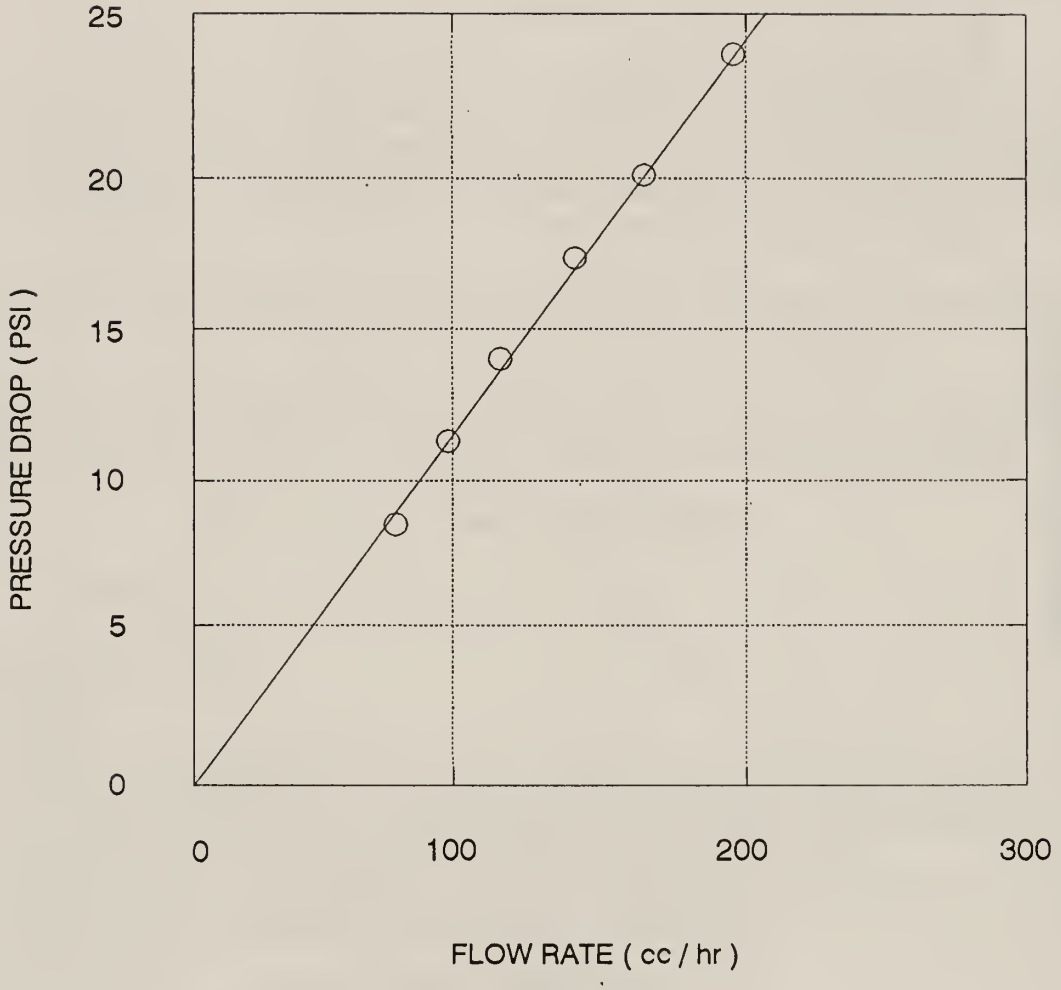
```
C       *  DIFLIB.FOR  *
C
      CHARACTER*8 FIN
      REAL N2
      DIMENSION P(12),STCC(12),SG(12),VO(12),WG(12),VL(12),VG(12),
     +DV(12),DP(12),ALDP(12),ALDV(12),ALVP(12),SQDP(12),VV(12),VR(12),
     +VGG(12),DL(12),VRT(12),VR1(12),VGIC(12),Z(12),VRT1(12),DL1(12),
     +GOR1(12),FM(12),S1(12),FMSG(12),S2(12),ASG(12),GFVF(12),
     +GFVF2(12),GEF1(12),GEF2(12),C(15),Y(15,15),TR(15),PR(15),CT(12),
     +CP(12),RP(4),RT(4),STCCT(12),GORSCF(12),STCC1(12)
      WRITE(*,3)
    3 FORMAT(2X,'***DIFFERENTIAL LIBERATION***'/)
      WRITE(*,4)
    4 FORMAT(1X,'FILE NAME : '$)
      READ(*,5)FIN
    5 FORMAT(A8)
      OPEN(9,FILE=FIN,STATUS='OLD')
      OPEN(12,FILE=' ',STATUS='NEW')
      READ(9,*)M,RST,VOD,SOD,PB,DSAT
      PB=PB*6.8946
      TC=(RST-32)*5./9.
      T=273.15+TC
      TF=RST
      DO 7 J=1,M
```



PD = 0.223 X FLOW RATE - 0.322

COIL CONSTANT = 0.289 / 0.223 = 1.296

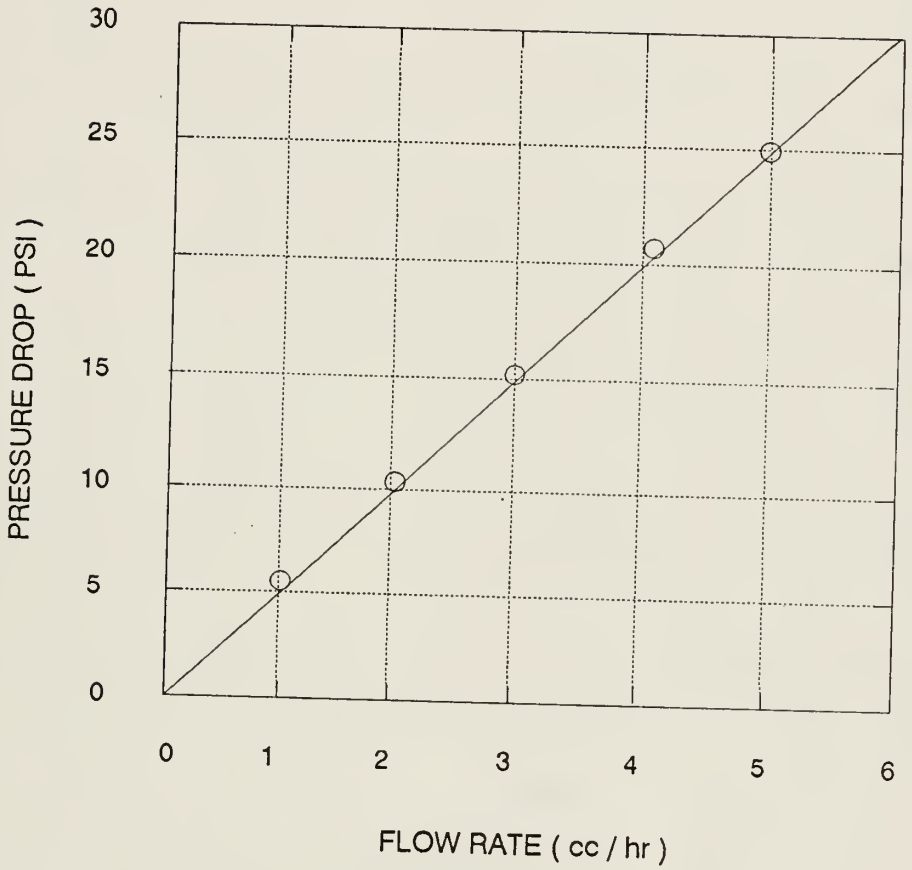
Figure 12. Calibration of 10 Ft. Capillary Coil



PD = 0.117 X FLOW RATE - 0.323

COIL CONSTANT = 0.289 / 0.117 = 2.55

Figure 13. Calibration of 5 Ft. Capillary Coil



PD = 9.88 X FLOW RATE - 0.800

COIL CONSTANT = 0.289 / 9.88 = 0.0293

Figure 14. Calibration of 20 Ft. Capillary Coil

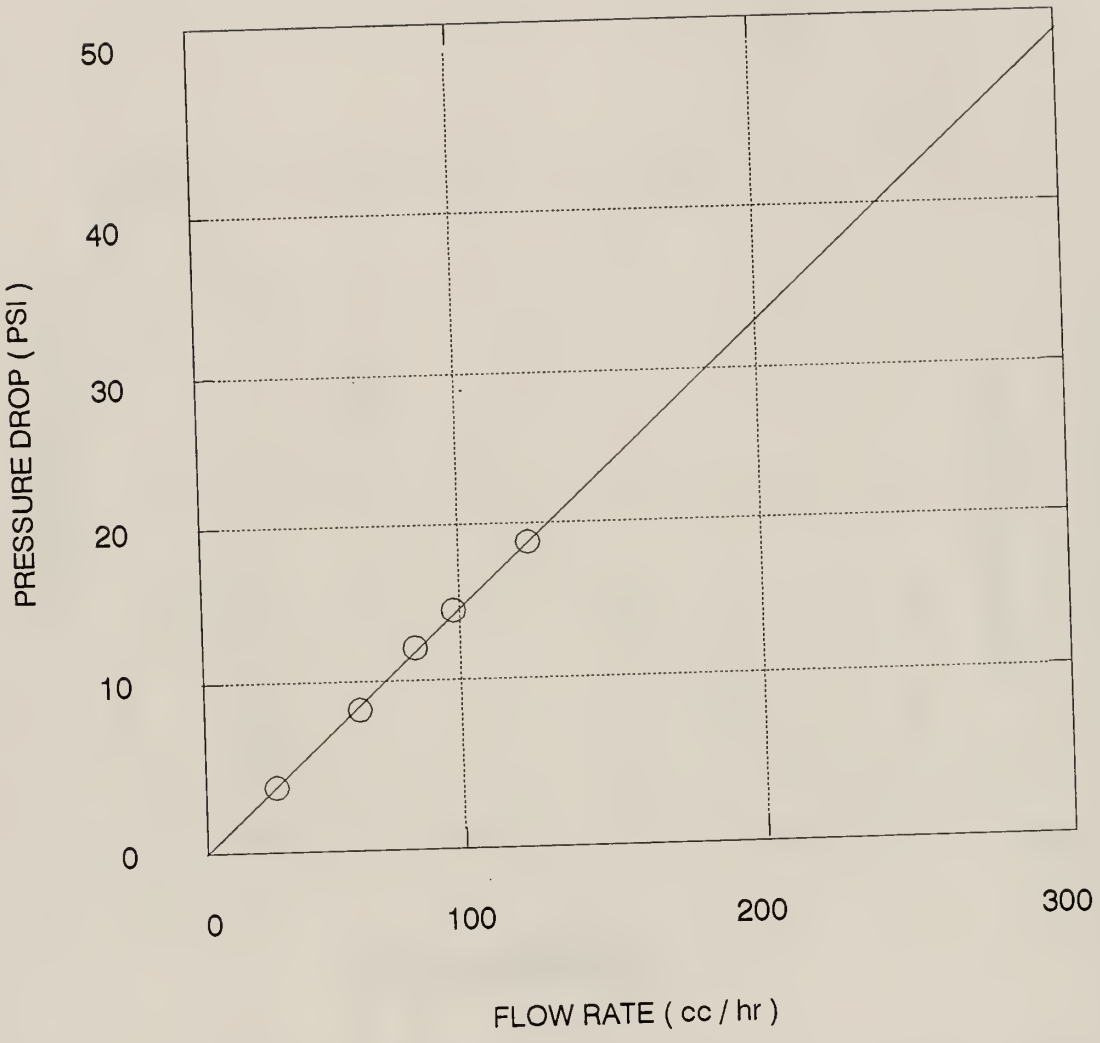


Figure 15. Viscosity of Hexane Saturated with C1

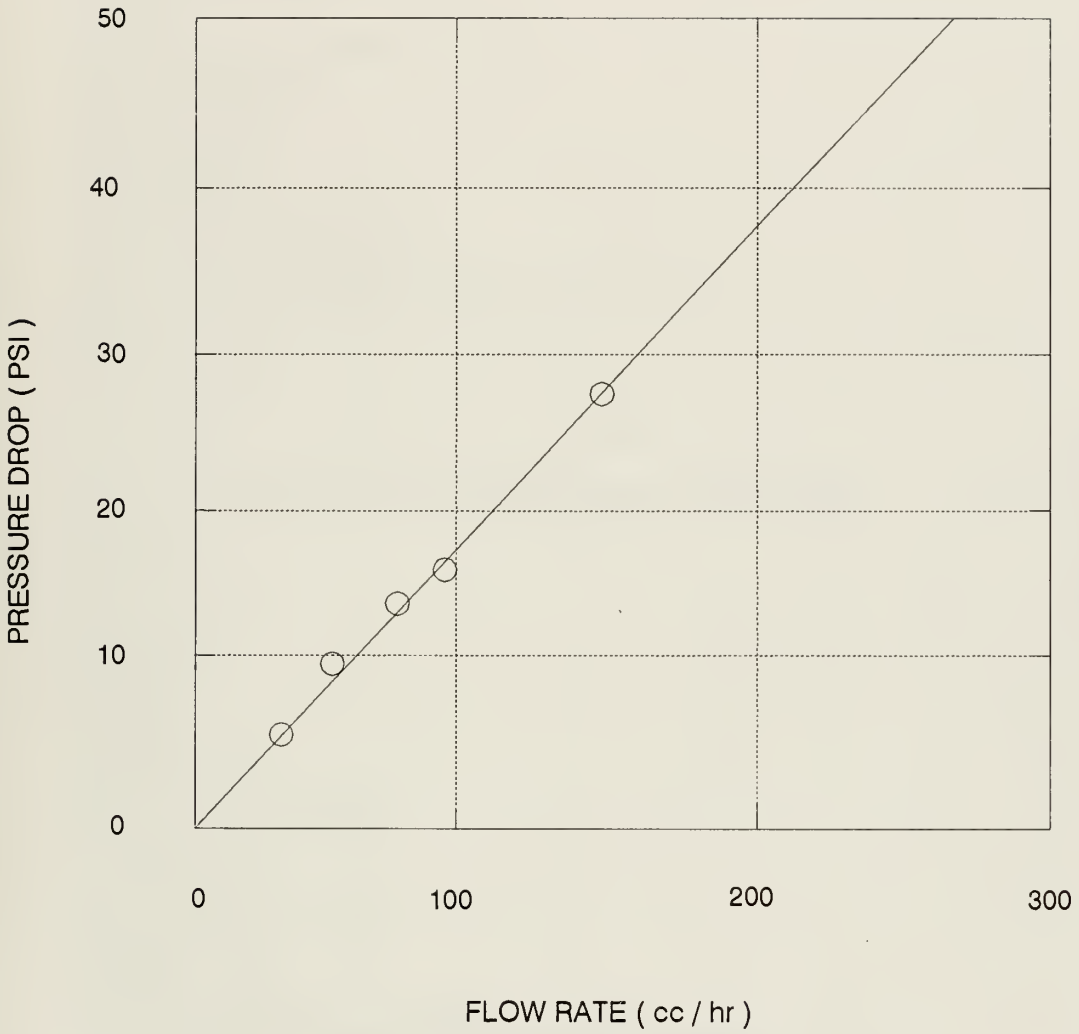


Figure 16. Viscosity of Hexane Saturated with C1

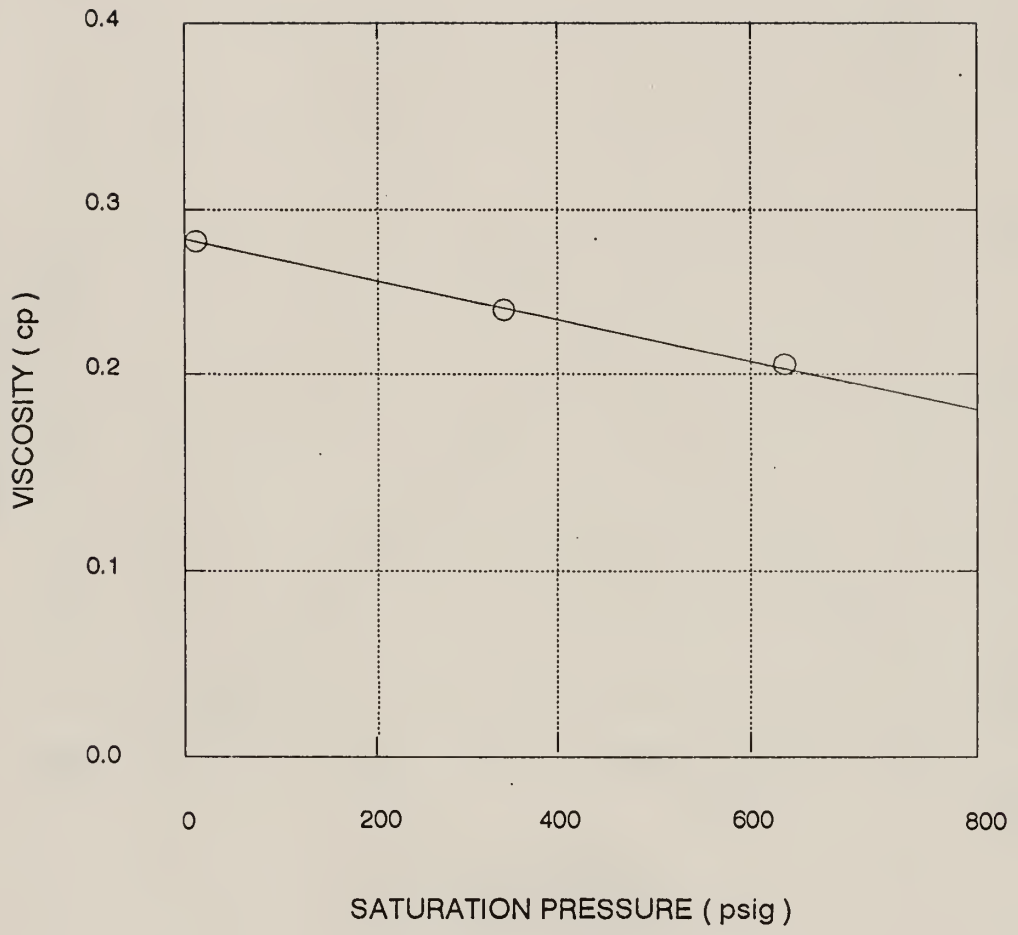


Figure 17. Viscosity of Hexane Saturated with C1

```
      READ(9,*)P(J),STCC(J),SG(J),VO(J),VG(J)
      READ(9,*)(Y(J,K),K=1,12)
      P(J)=P(J)*6.8946
      PI=P(J)
      IF(J.EQ.1)GO TO 13
      DO 16 K=1,12
      C(K)=Y(J,K)
   16 CONTINUE
      SMG=SG(J)
      WRITE(12,11)PI/6.8946
   11 FORMAT(/1X'PRESSURE='E15.8,2X,'PSIG')
      CALL PSCC(C,PI,PTR,PPR,T)
      TR(J)=PTR
      PR(J)=PPR
      CALL ZFCT(PPR,PTR,ZF)
      Z(J)=ZF
      CALL GVISCO(SMG,C(11),C(10),C(12),TF,PTR,PPR)
   13 SG(1)=0.0
      Z(1)=0.0
    7 CONTINUE
      CLOSE(9)
      STT=0.0
      STS=0.0
      DO 9 J=1,M
      STT=STT+STCC(J)
      VR1(J)=VO(J)/VOD
    9 CONTINUE
      STCCT(1)=STT/VOD
      DO 10 J=2,M
      STS=STS+STCC(J)
      STCCT(J)=(STT-STS)/VOD
      VRT1(J)=(STCCT(1)-STCCT(J))*VG(J)/STCC(J)+VR1(J)
   10 CONTINUE
      VRT1(1)=VR1(1)
C
      WOD=SOD*VOD
      WGG=0.0
      SLDV=0.0
      SLDP=0.0
      SLVP=0.0
      SSDP=0.0
      WMT=DSAT*VO(1)
      DL1(1)=DSAT
      DO 2 I=2,M
```

```
      WG(I)=STCC(I)*SG(I)*28.964/23631.
      WGG=WGG+WG(I)
      XWL=WMT-WGG
      DL1(I)=XWL/VO(I)
 2    CONTINUE
      WS=WOD+WGG
      VS=WS/DSAT
      DD=VO(1)-VO(M)
      PP=VS-VO(M)
      DO 33 I=2,M
      XV=(VO(1)-VO(I))*PP/DD
      VL(I)=VS-XV
      DV(I)=1.-VL(I)/VS
      DP(I)=PB-P(I)
      ALDP(I)=ALOG10(DP(I))
      ALDV(I)=ALOG10(DV(I))
      ALVP(I)=ALDV(I)*ALDP(I)
      SLDV=SLDV+ALDV(I)
      SLDP=SLDP+ALDP(I)
      SQDP(I)=ALDP(I)**2
      SLVP=SLVP+ALVP(I)
      SSDP=SSDP+SQDP(I)
 33   CONTINUE
      MM=M-1
      B=(SLVP*MM-SLDV*SLDP)/(MM*SSDP-SLDP*SLDP)
      A=(SLDV-B*SLDP)/MM
      WL=WS
      VST=0.0
      DO 44 I=2,M
      DV(I)=10.**A*(DP(I)**B)
      VV(I)=(1.-DV(I))*VS
      VR(I)=VV(I)/VOD
      VGG(I)=(VS/VO(1)*VO(I)+VG(I))-VV(I)
      WL=WL-WG(I)
      DL(I)=WL/VV(I)
      VST=VST+VGG(I)
      VRT(I)=VST/VOD+VR(I)
 44   CONTINUE
      SSTT=STT
      DO 19 I=1,M
      SSTT=SSTT-STCC(I)
      GOR1(I)=SSTT/VOD
 19   CONTINUE
      TM=STT/23631.
```

```
      SMF=0.0
      SMSG=0.0
      TASG=0.0
      DO 20 I=2,M
      FM(I)=(STCC(I)/23631.)/TM
      SMF=SMF+FM(I)
      S1(I)=SMF
      FMSG(I)=FM(I)*SG(I)
      SMSG=SMSG+FMSG(I)
      S2(I)=SMSG
      ASG(I)=S2(I)/S1(I)
      TASG=TASG+ASG(I)
      GFVF(I)=VG(I)/STCC(I)
      GFVF2(I)=(101.325/288.15)*Z(I)*T/P(I)
      GEF1(I)=1./GFVF(I)
      GEF2(I)=1./GFVF2(I)
 20   CONTINUE
      WRITE(12,100)RST
100   FORMAT(//20X'DIFFERENTIAL LIBERATION AT 'F6.2' F'//30X,
     +'EXPERIMENT DATA'//4X'PRESSURE'3X'OIL DENSITY'2X'DIF.OIL VOL.',
     +2X'DIF.TOT.VOL'2X'OIL VOL'2X'SOL.GOR'/)
      DO 22 I=1,M
      GORSCF(I)=GOR1(I)*5.615
      WRITE(12,105)P(I)/6.8946,DL1(I),VR1(I),VRT1(I),VO(I),GORSCF(I)
105   FORMAT(1X,E12.5,5X,F5.4,8X,F6.4,7X,F7.4,5X,F6.2,3X,F6.2)
 22   CONTINUE
      WRITE(12,110)
110   FORMAT(/5X'GAS GR'3X'CUM. GAS GR'2X'Z-FACT'2X'GAS FVF'2X,
     +'GAS EXP.F'/)
      DO 25 I=2,M
      WRITE(12,115)SG(I),ASG(I),Z(I),GFVF(I),GEF1(I)
115   FORMAT(1X,5(F10.4))
 25   CONTINUE
      WRITE(12,120)
120   FORMAT(//15X'SMOOTHED DATA'//2X'PRESSURE'3X'OIL DENSITY'2X,
     +'DIFF OIL VOL'2X'DIF.TOT.VOL'2X'OIL VOL'2X'SOL. GOR'/)
      DL(1)=DSAT
      VV(1)=VS
      VR(1)=VS/VOD
      VRT(1)=VR(1)
      DO 17 I=1,M
      WRITE(12,125)P(I)/6.8946,DL(I),VR(I),VRT(I),VV(I),GORSCF(I)
125   FORMAT(1X,E12.5,6X,F5.4,8X,F6.4,5X,F7.4,7X,F7.3,3X,F6.2)
 17   CONTINUE
```

```
      WRITE(12,130)
130   FORMAT(/5X'GAS GR'3X'CUM. GAS GR'2X'Z-FACT'2X'GAS FVF'2X,
     +'GAS EXP.FACTOR'/)
      DO 8 I=2,M
      WRITE(12,135)SG(I),ASG(I),Z(I),GFVF2(I),GEF2(I)
135   FORMAT(1X,4(F10.4),6X,F6.2)
 8    CONTINUE
      CLOSE(12)
      STOP
      END
C
      SUBROUTINE GVISCO(G,N2,CO2,H2S,T,TPR,PPR)
      DIMENSION RP(4),RT(4),A(18)
      REAL N2
      A(1)=-2.4621182
      A(2)=2.97054714
      A(3)=-2.8624054E-1
      A(4)=8.05420522E-3
      A(5)=2.80860949
      A(6)=-3.4980335
      A(7)=3.60373020E-1
      A(8)=-1.04432413E-2
      A(9)=-7.93385684E-1
      A(10)=1.39643306
      A(11)=-1.49144925E-1
      A(12)=4.41015512E-3
      A(13)=8.39387178E-2
      A(14)=-1.86408848E-1
      A(15)=2.03367881E-2
      A(16)=-6.09579263E-4
      Q=ALOG10(G)
      VUC=(1.709E-5-2.062E-6*G)*T+8.188E-3-6.15E-3*Q
      CN2=N2*(8.48E-3*Q+9.59E-3)
      CCO2=CO2*(9.08E-3*Q+6.24E-3)
      CH2S=H2S*(8.49E-3*Q+3.73E-3)
      VIS1=VUC+CN2+CCO2+CH2S
      IF(PPR.LT.1.)GO TO 111
      DO 40 I=1,4
      RP(I)=PPR**(I-1)
      RT(I)=TPR**(I-1)
 40   CONTINUE
      TEMP=0
      K=0
      DO 10 J=1,4
```

```
      SUM=0
      DO 20 I=1,4
      SUM=SUM+A(I+K)*RP(I)
 20   CONTINUE
      TEMP=TEMP+SUM*RT(J)
      K=K+4
 10   CONTINUE
      RATIO=EXP(TEMP)/TPR
      GO TO 222
111   RR=(2.97689E3*EXP(-8.5*TPR)+0.017604)/6.23306953E-1
      RATIO=RR*(1.608919E-2*EXP(3.7*PPR)-0.02596472)+1.0
      IF(RATIO.LT.1.)RATIO=1.0
      GO TO 222
222   GVIS=RATIO*VIS1
      WRITE(12,600)RATIO
600   FORMAT(1X,'VISCOSITY RATIO (VG/V1) ='E15.8)
      WRITE(12,300)GVIS
300   FORMAT(1X,'GAS VISCOSITY ='E15.8)
      RETURN
      END
C
      SUBROUTINE ZFCT(P,T,Z)
      A=1.39*SQRT(T-.92)-0.36*T-0.101
      B1=(0.62-0.23*T)*P
      B2=(0.066/(T-0.86)-0.037)*P**2
      B3=0.32/10.**(9.*(T-1))*P**6
      B=B1+B2+B3
      C=0.132-0.32*ALOG10(T)
      D1=0.3106-0.49*T+0.1824*T**2
      D=10.**D1
      Z=A+(1-A)/EXP(B)+C*P**D
      WRITE(12,200)Z
200   FORMAT(1X'Z-FACTOR= 'E15.8)
      RETURN
      END
C
      SUBROUTINE PSCC(C,P,PTR,PPR,T)
      REAL N2
      DIMENSION C(14),CT(12),CP(12)
      CT(1)=344.
      CT(2)=550.
      CT(3)=666.
      CT(4)=733.
      CT(5)=766.
```

```
      CT(6)=830.
      CT(7)=847.
      CT(8)=915.
      CT(9)=1025.
      CT(10)=548.
      CT(11)=227.
      CT(12)=672.
      CP(1)=673.
      CP(2)=709.
      CP(3)=618.
      CP(4)=530.
      CP(5)=551.
      CP(6)=482.
      CP(7)=483.
      CP(8)=434.
      CP(9)=370.
      CP(10)=1073.
      CP(11)=492.
      CP(12)=1309.
      TPM=0.0
      PPM=0.0
      DO 2 I=1,12
      TPM=TPM+CT(I)*C(I)
      PPM=PPM+CP(I)*C(I)
    2 CONTINUE
      E=120.*((C(10)+C(12))**.9-(C(10)+C(12))**1.6)+15.*(C(10)**.5
     +-C(12)**4)
      PTC=TPM-E
      PPC=PPM*PTC/(TPM+C(12)*(1.-C(12))*E)
      PTC1=PTC/1.8
      PPC1=PPC*6.895
      PTR=T/PTC1
      PPR=P/PPC1
      RETURN
      END
```

Format for Data Entry for DEFLIB.FOR

Input data format for DIFLIB.FOR

1. No. of Step, Tres(F), Vod, Dod, Psat, Dsat

2. Pres(psi), Vgas(St), Gas Gr., Voil, Vgas(res)

3. Mole fraction of C1,,C2, C3, C4, C5, C6,C7+ C02,N2,H2S

4. Pres(psi), Vgas(St), Gas Gr., Voil, Vgas(res)

5. Mole fraction of C1,,C2, C3, C4, C5, C6,C7+ C02,N2,H2S

6. Pres(psi), Vgas(St), Gas Gr., Voil, Vgas(res)

7. Mole fraction of C1,,C2, C3, C4, C5, C6,C7+ C02,N2,H2S

8. Pres(psi), Vgas(St), Gas Gr., Voil, Vgas(res)

Repeat step 3 and 4 for the required number of pressure step-times.

Note: Tres(F) =Reservoir temperature in degrees F
Vod =Residual oil volume at standard condition
Dod =Residual oil density at standard condition
Psat =Saturation pressure
Dsat =Density of saturated oil at reservoir condition

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Steve S.K. Sim

Objectives/Purposes: Study phase behavior relationships of oil and gas to determine thermodynamic and transport properties under varying conditions.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 22 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
PVT	By field or project, e.g. Energy Field or MCA study	in IP PVT publications	Sim PVT	Sim

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

ROUTINE RESISTIVITY MEASUREMENTS

Emmanuel O. Udegbunam

To Zero Resistivity Meter

1. Select MEASURE (Press FUNCTION key)
2. Select TRIGGERED mode (Press MEASURE mode key)
3. Connect cables (MUST be open-circuited...)
4. To zero "0000", press Cs/D key
5. Press these keys: [1][6][8][9] [=] **[shift][open]** "GO" light comes on.
6. Press START - "GO" light disappears.
7. Wait for "GO" to light again.

Cable Hook-Up

Color band on Cable	**Cable Ports on Equipment**		
	Meter	**Cell**	**Coreholder**
BLACK	IL	CA	Black
BLACK & WHITE	PL	PA	Blue
RED & WHITE	PH	PB	Green
RED	IH	CB	Red

To Measure Resistance With Meter

1. Press [Rs/Q]
2. Select SERIES (press **[EQUIVALENT CIRCUIT]**
3. Place DUT (device under test) in test fixture (e.g. core in coreholder or brine in resistivity cell).
4. Press **[START]**
5. RLC display shows resistance in Ω or kΩ.

To Measure Brine Resistivity

1. Place suction tube in brine to be measured (inside a beaker) and open valve.

2. **First flush the cell:** Pull syringe plunger up until brine covers electrodes. Displace brine into another container by pushing syringe plunger down. Repeat process three times.

3. **To make resistance (r_w) measurement:** Connect color-coded cables as described above. Fill cell with brine until all electrodes are covered. Operate the resistivity meter.

   Measure r_w and brine temperature (by flipping the switch).

4. **To calculate brine resistivity:**

   $$Rw = 0.002 \times r_w \text{ (ohm-m)}$$

To Measure Core Resistivity, R_o

1. Wet end pads (on the core holder electrodes) with brine saturating the core sample.
2. Place pre-saturated core sample into core holder and fasten.
3. Connect color-coded cables appropriately.
4. Measure core resistance, r_o at the meter (press START).
5. Calculate core resistivity:

   $$R_o = r_o \times \pi d^2 / 400L \text{ (ohm-m)}$$

where:

R_o = resistivity in ohm-meters
d = core diameter in cm
L = core length in cm
r_o = resistance in ohms.

To Determine Formation Factor

$$F = R_o / R_w \text{ (dimensionless)}$$

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Emmanuel O. Udegbunam
Dennis J. Haggerty

Objectives/Purposes: To measure electrical resistivity on core for use in Log calculations (e.g., formation factor).

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Resistivity	(routine)	in certain publications (IP series)	NA	NA

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

SAMPLING OF RESERVOIR FLUIDS FOR GEOCHEMISTRY

Ilham Demir

Sampling reservoir fluids requires careful and well thought out procedures to determine or estimate as closely as possible the chemical conditions in reservoir rocks. Field measurements include the determination of temperature, conductivity, oxidation-reduction potential (Eh), and pH. This procedure is based largely on one developed by the USGS (Lico et al., 1982, Methods for collection and analysis of geopressured geothermal and oil field waters, USGS Water Supply Paper 2194).

Apparatus, Reagents, and Equipment

1. Two-gallon carboy with bottom spigot.
2. Polyethylene column filled with glass wool.
3. Multiprobe monitoring chamber, with bottom inlet and top outlet for continuous flow; polycarbonate.
4. Bottles, polyethylene and glass.
5. Tubing, flexible PVC and tygon (also polyethylene and/or vinyl used to accomplish well-head connections with the help of hose clamps).
6. Graduated cylinder and pipets.
7. Nitric acid (doubly distilled).
8. pH buffer solutions.
9. Automatic pump, Cole-Parmer Master Flex, Model 7533-20.
10. In-line filter holder, 142 mm diameter, polycarbonate.
11. Membrane filter, 142 mm diameter, 0.1-μm and 0.45-μm pore size.
12. Ice box and ice to store the samples.
13. Conductance/resistance meter with conductance cell and temperature probe, YSI Model 34.
14. pH meter with temperature probe and pH and Eh electrodes, Orion Model SA 250.

15. Field data forms (a copy is attached).

Precautions

Formation fluids are under high pressure at oil well heads. Goggles, heavy duty rubber gloves and a lab coat must be worn during sampling, as well as when samples are acidified with concentrated HNO_3. If the sampling valve is directly under the pump jack a hard hat must be worn during sampling. When hoses need to be disconnected and valves opened, it should be done gradually and slowly to minimize splashing of formation fluids.

Procedure

All the sampling bottles are prewashed with 10-percent nitric acid and rinsed with deionized water. Samples are collected at the well head and isolated from the atmosphere as much as possible to minimize oxidation and degassing.

1. Attach the PVC tubing to the bleeding line at the well head, open the bleeding valve slowly, and rinse the tubing and the carboy well at least once with the formation fluid.

2. Insert the other end of the tubing all the way down to the bottom of the carboy through a hole in the cap. Fill the carboy with formation fluid and quickly replace the cap and the tubing with an air-tight cap to minimize oxidation and degassing.

3. Allow sufficient time for the oil and water to separate. This usually takes from 5 to 30 minutes. When separation occurs, the brine zone below the oil-brine line on the carboy wall looks light and the oil zone above it looks dark.

4. Connect the spigot of the carboy to the polyethylene column (filled with glass wool) with PVC or tygon tubing. Connect the other end of the column to the inlet of the pump and the outlet of the pump to the inlet of the multiprobe monitoring chamber using tygon tubing.

5. Calibrate and place the electrodes in the multiprobe monitoring chamber. Open the valve of the carboy spigot and pump the brine through the glass wool column into the multiprobe chamber. The glass wool removes any solids and oil droplets. When the brine begins overflowing from the chamber, start monitoring the pH, Eh, conductivity, and temperature under continuous flow conditions. The pH is recorded under slow and Eh under fast flow conditions. Record the values when the readings are stable and then turn off the pump and close the carboy valve.

6. Disconnect the tygon tubing from the multiprobe monitoring chamber and connect it to the inlet of the in-line filter assembly holding 0.1-μm membrane filter. Pump

about 1-L brine, discarding the first 250 ml and collecting the rest in a polyethylene bottle. Rinse all the sampling bottles twice with the collected water. Then pump 250-ml brine in to the polyethylene bottle and close the carboy valve. Acidify 125-ml of it with nitric acid to pH <1.5 in a separate polyethylene bottle, label it as filtered acidified (FA), and store it on ice for cation analyses. Make 1:4 and 1:1 dilutions on the rest of the sample, label them as such and store them in 125-ml polyethylene bottles for silica analyses.

7. Replace the 0.1-μm membrane filter with a 0.45-μm membrane filter. Open the carboy valve, pump about 250 ml water to rinse the filter, and then collect 1-L brine sample. Label this as filtered (F) and store it on ice for anion analyses.

8. Collect oil sample from the carboy and store it in a 125-ml glass bottle with a teflon-lined cap.

9. To prepare the for the next sample, rinse the multiprobe chamber and the in-line filter holder thoroughly with deionized water and repeat steps 1 through 8; use a clean carboy and tubing, new glass wool columns and membrane filter for each sample.

10. Discard unused brine/oil mixtures in a nearby storage tank.

11. Transport all the samples in the ice box to the laboratory.

Calculations

Because we use a conductivity cell with a cell constant of 10.0/cm the conductivity readings should be multiplied by 10 and resistivity readings are to be divided by 10. The data sheets are presently stored in the Natural Resources Building, Room 217 (example data sheet on next page).

Precision and Accuracy

Before each field trip the conductivity cell and meter are tested with 10,000 mg/L and 150,000 mg/L NaCl solutions and the results are compared with a plot of a resistivity (or conductivity) vs NaCl concentration (fig. 18) as reported in the literature (Collins, 1975, Geochemistry of oil field brines, p. 33, Elsevier, New York). Accurate results should be obtained each time. Reference filling solutions for pH and Eh electrodes are changed before each field trip. The pH electrode is calibrated in the field with pH 4 and pH 7 buffer solutions before each use. Automatic temperature compensation is used so that the pH and conductivity values are reported at 25°C.

Specifications, including accuracy, of each instrument and electrode are listed in their respective manuals, which are kept in room 31. A list of the manuals and page numbers where the information is reported are listed below:

YSI Model 34 Conductance-Resistance Meter Instruction Manual, p. 2.
ORION SA 250 p pH Meter Instruction Manual, p. 13.
ORION Ross Sure-Flow Electrodes Instruction Manual, p. 16.
ORION Platinum Redox Electrodes Instruction Manual, p. 13.
CORNING pH Combination Electrodes, a single information card. This electrode is taken to the field also, as a spare electrode.

ISGS FIELD DATA SHEET FOR OIL AND BRINE SAMPLES

DATE :

API NO. :

FIELD NAME :

OPERATOR :

WELL NAME :

LOCATION : T ____ R____ SEC____ ¼ SEC_____

PRODUCING FORMATION :

PERFORATION DEPTH (ft) :

SURFACE ELEVATION (ft) :

WATER-FLOODED? : Y____ N____

MEASUREMENTS MADE FOR BRINE AT THE WELL HEAD:

TEMPERATURE (°C)

CONDUCTIVITY : Cell Constant = 10/cm

WITH ATC_____ x 10

WITHOUT ATC_____ x 10

RESISTIVITY : WITHOUT ATC_____ x 10

Eh (mV) :

pH :

SAMPLES COLLECTED BY :

BRINE SAMPLE NO. : EOR-B_____

OIL SAMPLE NO. : EOR-O_____

COMMENTS:

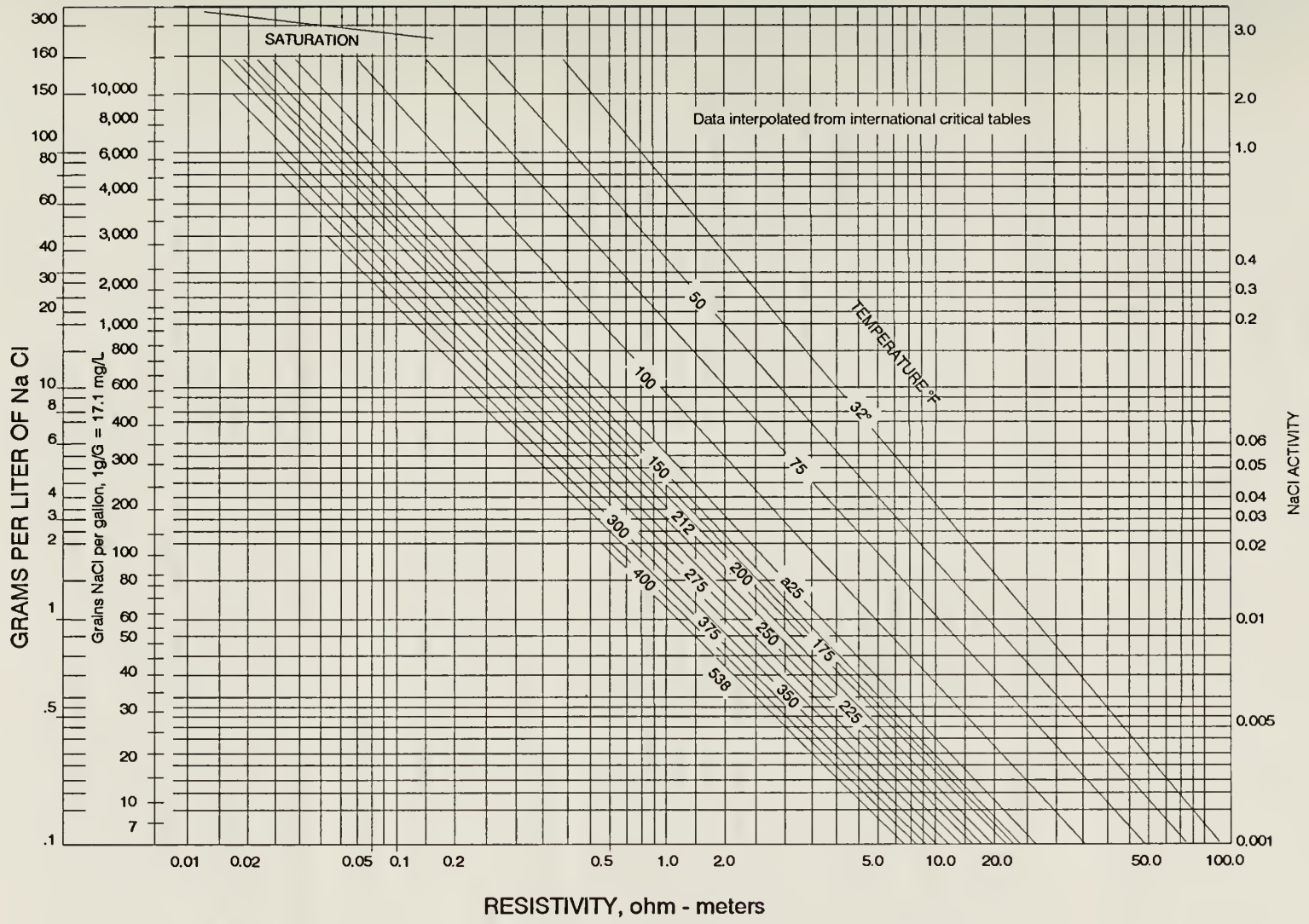


Figure 18. Plots of Resistivity of Aqueous Solutions Containing Various Concentrations of Sodium Chloride

Because the brines are predominantly NaCl solutions, Na and Cl concentrations reported by the laboratories are checked against conductivities we measure in the field. The relation between the Na and Cl concentrations and the conductivity should be similar to that (fig. 18) reported in the literature (Collins, 1975, Geochemistry of oil field brines, p. 33, Elsevier, New York). Also the NaCl contents of brines in the Illinois Basin generally tend to increase with depth (see Meents, et al., 1952, ISGS Illinois Petroleum 66; Graf et al., 1966, ISGS Circular 397). Therefore, the Na and Cl concentrations are also compared to the depth of samples to see whether they follow the general trend. Other elemental concentrations are also checked to see if they are within the ranges reported in the literature.

In addition to the above steps, prepare artificial brines and submit them to the analytical laboratories for analysis as blind samples. Submit one blind sample for at least every other sample batch.

The field and laboratory data on the samples are kept in a folder located in Room 217 at the Survey. The field data include date of collection, API number, field name, operator name, well name, location, producing formation, perforation depth, surface elevation, water-flooding information, temperature, conductivity, resistivity, Eh and pH measurements. Laboratory data on brine samples includes concentration of seven anions and about thirty cations. The oil data include percentages of four hydrocarbon fractions (saturates, aromatics, resins, asphaltenes, lost or light hydrocarbons) and ratios of C_{17}/C_{18}, pristane/phytane, pristane/C_{17}, and phytene/C_{18}. The field and laboratory data are also entered regularly into a computer as Lotus 123 files under the subdirectory OILGAS. The computer with the files is presently located in Room 217, Illinois State Geological Survey.

Procedure for Cleaning Carboys

1. Rinse with gasoline to remove oil and sludge.

2. Place carboy under a fume hood for at least 30 minutes until dry.

3. Rinse carboy with warm water.

4. Fill carboy with warm water, add dishwashing detergent and brush inside walls

5. Rinse with warm water.

6. Fill carboy with warm water, add dishwashing detergent and let it soak for at least 4 hours.

7. Brush and rinse carboy with warm water.

8. Fill carboy with warm water, add dishwashing detergent and brush inside walls.

9. Rinse thoroughly with warm water.

10. Rinse with distilled water.

11. Rinse with deionized water.

12. Clean carboy spigots and caps and other sampling equipment that are stained with oil by using the above procedure.

Procedure for Cleaning Sample Bottles

1. Rinse each polyethylene bottle with 10% distilled HNO_3. Use approximately 15 ml of 10% HNO_3 for 125 ml bottles, and 100 ml for 1000 ml bottles.

2. Rinse each bottle at least two times with deionized water using at least the same amounts as above.

3. Rinse the glass bottles with deionized water.

Analyses of Brine Samples

The samples were analyzed at the ISGS for 27 elements using inductively coupled plasma spectroscopy. Anion and NH_4+ analyses of the samples were carried out at ARDL Laboratoies, Mt. Vernon, Illinois, using standard ASTM-EPA procedures.

Selected analytical procedures used by the two laboratories follow.

Analysis of Brines for Cations by Inductively Coupled Plasma Spectroscopy

Scope and Use of Method

Inductively Coupled Plasma Spectroscopy (ICP) is appropriate for the determination of a large number of elements in aqueous or organic solutions. The analysis of solid samples is possible if the sample can be dissolved, although analytical methods for the ICP analysis of dissolved solid samples have not yet been optimized at ISGS. ICP is most appropriate when the determination of a large number of constituents is desired in relatively dilute solutions. The following is a list of those constituents which are currently available for analysis: (Ag), Al, As, B, Ba, Be, (Bi), Ca, Cd, Co, Cr, Cu, Fe, (Ge), (Hg), (In), K, La, (Li), Mg, Mn, Mo, Na, Ni, (P), Pb, Rb, (S), Sb, Sc, Se, Si, Sn, Sr, (Te), Ti, Tl, V, Zn, Zr. Those constituents in parenthesis are not currently reported for routine determinations.

General Principle(s) or Summary of the Method

An ICP source consists of a quartz tube, or "torch", through which a flow of ionized argon gas is passed. The torch is surrounded by a water-cooled coil through which a radio frequency electric field is passed. The gaseous plasma is sustained by continuing ionization of argon by inductive coupling of the ionized gas with the high-frequency field. A sample aerosol is generated through the use of an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the plasma, in which the constituent atoms are subjected to temperatures of about 6000°C. Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma efficiently produces both atomic and ionic emission spectra, the intensity of which are measured by a polychromator with multiple fixed exit slits and corresponding photomultiplier tubes. The intensities of the emission spectra, as recorded by the photomultiplier tubes, are proportional to the concentrations of the atoms in the sample being analyzed.

Equipment, Apparatus and Reagents

Model 1100 Thermo Jarrell-Ash Inductively Coupled Argon Plasma Spectrometer housed at the Illinois State Water Survey. Instrument control, automatic background correction, and spectral interference correction are performed by using an IBM personal computer and appropriate vendor software.

Single element stock solutions are purchased or prepared from spectroscopically pure metals or high-purity metal salts. Mixed calibration standards are made from the single element stock solutions. The matrix of each mixed standard and sample may include 100 μg/mL Te as an internal standard to correct for variations in instrument sensitivity, electronic drift, nebulizer efficiency, total salt content, and other matrix effects.

Reference Standards: Reference standards of known concentration may be obtained from Spex Industries, Inc., 3880 Park Avenue, Edison, New Jersey 08820 (QCS-ICP-7) and National Bureau of Standards (SRM 3171 and SRM 3172). The acid content of the reference standards and samples should be the same.

Procedure

The Shared Equipment Agreement between the three surveys requires that only factory-trained personnel operate the ICP.

The procedures described below are somewhat generic in nature with respect to the computer system which operates the instrument, acquires the data, performs background and spectral interference corrections, performs the calibration and calculates the final concentrations.

Preliminary Considerations

Before routine analyses can be performed, information must be gathered which will be used to determine the conditions under which the analyses are to be performed. Among the factors which must be evaluated are: 1) what elements are to be determined, 2) whether and how background corrections are to be made for each constituent to be determined, and 3) whether and how inter-element interferences are to be corrected. As the above criteria are determined, they are incorporated into the Analytical Control Table (ACT) which provides any necessary information to operate the spectrometer and perform the analyses.

Which elements are to be determined is limited by what elements are available on the instrument. The list of elements and their wavelengths in nanometers includes: Ag (328.0), Al (308.2), As (193.6), B (249.6), Ba (493.4), Be (313.0), Bi (223.0), Ca (317.9, 393.3), Cd (228.8), Co (228.6), Cr (267.7), Cu (324.7), Fe (259.9, 271.4), Ge (209.4), Hg (184.9), In (203.6), K (766,4), La (408.6), Li (670.7), Mg (279.5, 383.2), Mn (257.6), Mo (202.0), Na (330.2, 588.9), Ni (231.6), P (214.9), Pb (220.3), Rb (780.0), S (180.7), Sb (206.8), Sc (361.3), Se (196.0), Si (288.1), Sn (189.9), Sr (421.5), Te (214.2), Ti (334.9), Tl (190.8), V (292.4), Zn (213.8), and Zr (339.1). After the list of elements to be analyzed has been determined, it must be decided how they are to be arranged in the calibration standards. Under the current system, seven standards are permitted with one being a blank. Factors to be considered in the arrangement of the elements in the standards are: combine similar anions and acids and avoid combinations where there could be spectral interferences. This basic information is incorporated into an ACT.

A determination must be made concerning which elements will require background correction and how that correction will be performed. Test samples must be chosen which will be representative of the types of samples which will be analyzed and should be in the same solution matrix as the samples. Also included in the evaluation should be a reagent blank, and a standard at a concentration of approximately 100 times the detection limit. The test samples, blank, and standard are then scanned for each element. The scan represents a graphical output of the emission spectrum around the analytical wavelength of the element under consideration. In general, background correction should be applied where: 1) line-to-background ratio is low (< 50%) with little spectral interference, 2) wavelengths below 250 nm at low concentrations, 3) where the emission line is in the vicinity of strong molecular band emission, 4) samples exhibit small localized changes in background compared to standards, and 5) the analyte line is near strong lines of a matrix component. Based on these criteria, an evaluation is made of whether background correction is necessary. If correction is required, a determination is made of which side of the line or both to correct on, and how far from the line the correction will be made. This background information is incorporated into the ACT.

The scan plots obtained above may be used for the preliminary evaluation of the presence of spectral interferences. The quantitative determination of spectral

interferences is obtained by analyzing spectroscopically pure (free of contaminants) solutions of each potential interferant at a concentration of 1000 mg/L. All analytical conditions except for inter-element corrections have been incorporated into the ACT and the instrument has been standardized using the calibration standards derived from above. Each potential interferant is analyzed allowing sufficient flush time with a reagent blank between interferant solutions to insure that no interferant remains in the nebulizer/torch system. The concentration of each element is examined to obtain its apparent concentration due to the presence of the interferant. the interference corrections are calculated as follows:

$$\text{Correction factor} = \frac{\text{apparent concentration of affected element}}{\text{concentration of interfering element}}$$

The significance of the correction factor and whether or not it should be entered into the ACT must be evaluated by considering the relative concentrations of the affected and affecting elements in the samples. Care should be taken to look for "domino-effect" interferences where one element affects a second element, and the second element, in turn, affects a third element. Interferences must be entered into the ACT such that the greatest interference is entered first.

Routine Analyses

Lighting torch: turn on water pump, the following toggle valves are on: torch, auxiliary, and sample. Wait 15 to 30 minutes. Turn the purge and auxiliary toggle valves off and use the needle valve labeled "sample" to turn sample gas flow off. Push "RF power" on. Turn power to approximately 0.5 kW forward power. Press the igniter button briefly and listen for ignition. When ignition is heard, turn power all the way on and at the same time turn auto power control on. Open "sample" needle valve slowly to 0.6 and turn peristaltic pump on. Allow torch to warm up at least 30 minutes.

Profiling the Hg channel: Profiling is a means of checking the alignment of a spectral line on the center of its exit slit. Log on to the computer and call the program which performs samples analysis (SAT in the current system). Issue the profile command (PF) and enter the physical channel number (PCN) 13 for Hg. Move the Hg lamp into position and rotate the micrometer knob until the monitor meter begins to register. Continue to rotate the micrometer until the meter reads 80% of full scale and record the micrometer reading. Continue to rotate the micrometer in the same direction until the meter reading begins to drop and again stop when the meter reads 80%. Take the average of this and the previous micrometer reading and adjust the micrometer to the average. Turn off the profile function. Record the profile value and temperature in the log book. Repeat if the analysis period extends beyond four hours.

Standardization: Call up the appropriate ACT to be used for the samples being analyzed. Initiate the standardization routine. Issue the necessary commands for the computer to perform the standardization and analyze each standard in the order established in the ACT (see Table 4). When all standards have been analyzed, issue the commands to calculate the regression coefficients and write them to the ACT. Terminate the standardization routine. Repeat the analysis of the standards as samples and verify that the concentrations are within acceptable limits of the expected concentrations. If necessary, repeat the standardization procedure. Reference standards should be analyzed next to verify that the observed concentration agrees with the expected concentration. If the observed concentrations do not agree with the expected concentrations, the source of the error (background, spectral, contamination, instrument settings, etc.) must be determined and corrected and the standardization repeated. After all conditions are optimized, the analyses may begin.

Table 4 - Calibration Standards

Calibration Standard 0 - Blank

Calibration Standard 1 - 10 ppm
Sb, Ba, Cd, Ca, Co, Cu, Pb, Mg, Mn, K, Sr, Zn

Calibration Standard 2 - 10 ppm
Al, Be, Fe, Ni, Na, Tl, Zr

Calibration Standard 3 - 10 ppm
As, B, Cr, Mo, Se, Si

Calibration Standard 4 - 10 ppm
La, Hg, Rb, Sc, Ti, V

Calibration Standard 5 - 100 ppm
Ca, Mg, Na, K

Analysis: sample reagent blanks should be analyzed along with samples and correction for contamination due to the blank should be made if necessary by loading the results of the blank analysis into a blank array. During the analysis of the samples, be sure to turn on the blank subtraction facility, where necessary. The analyses should represent multiple burns of the sample solution. The mean, standard deviation, and relative standard deviation of the multiple burns is calculated by the computer. Replicates should be run at the rate of 20% of the number of samples and a calibration check solution should be run every 20 samples. If necessary, repeat the calibration procedure if drift is detected. At least one set of reference standards should be run with each sample set. If the concentrations of some major constituents fall outside the linear limit of calibration, as shown in Table 5, the sample should be diluted, maintaining the original acid content.

Calculations

All calculations are performed by the computer system. If dilutions of the samples is required, the Dilution Factor routine may be used to calculate the concentration in the undiluted sample.

Precision and Accuracy

The accuracy and precision of a typical ICP method is shown in Table 5. Results are shown in Table 6.

Table 5. Typical ICP Analytical Limits

Element	Wavelength (nm)	Solution Detection Limit (mg/L)	Linear Limit (mg/L)
Al	308.2	0.09	1000
Sb	206.8	0.064	1000
As	193.6	0.106	1000
Ba	493.4	0.005	500
Be	313.0	0.0006	150
Bi	223.0	0.068	100
B	249.6	0.008	500
Cd	228.8	0.01	1000
Ca	393.3	0.005	20
"	317.9	0.05	1000
Cr	267.7	0.014	1000
Co	228.6	0.014	1000
Cu	324.7	0.011	500
Fe	259.9	0.012	150
"	271.4	0.1	1000
La	408.6	0.002	1000
Pb	220.3	0.084	1000
Mg	279.5	0.002	25
"	383.2	0.05	1000
Mn	257.6	0.004	500
Hg	184.9	0.02	1000
Ni	231.6	0.03	100
K	766.4	12	1000
Rb	780.0	2	10000
Sc	361.3	0.003	1000
Se	196.0	0.15	1000
Si	288.1	0.1	750
Ag	328.0	0.014	1000
Na	588.9	0.058	150
"	330.2	2	5000
Sr	421.5	0.0015	500
Tl	190.8	0.08	1500
Ti	334.9	0.008	300
V	292.4	0.015	500
Zn	213.8	0.004	500
Zr	339.1	0.015	500

Table 6. ICP QA/QC Results

	QA/QC Samples		Sample		
Element	Det.lim.[1]	% Bias[2]	Count	Coef.var.	RPD[3]
Al	0.027	7.43	6	3.75	2.8
As	0.156	4.82	5	3.10	22.2*
Ba	0.001	3.45	6	4.45	11.0
Be	0.001	6.02	6	6.59	15.6
B	0.015	4.20	4	4.44	1.6
Ca	0.029	3.45	6	3.05	2.8
Cd	0.010	6.00	6	1.44	<
Co	0.010	2.67	6	2.97	<
Cr	0.005	4.70	6	2.71	6.6
Cu	0.002	3.50	6	3.14	12.9
Fe	0.001	7.48	6	7.66	9.5
Hg	0.021	-	-	-	2.0
K	0.792	12.74	5	16.68	4.6
La	0.006	-	-	-	<
Mg	0.016	4.42	5	4.63	11.4
Mn	0.001	2.70	6	2.66	1.7
Mo	0.016	8.97	4	6.27	3.7
Na	0.019	6.81	5	9.70	7.6
Ni	0.030	6.68	6	7.33	11.0
Pb	0.045	5.30	6	3.35	22.2*
Rb	2.166	-	-	-	<
Sb	0.146	8.93	4	11.03	<
Sc	0.001	-	-	-	<
Se	0.041	5.18	5	5.64	5.5
Si	0.016	6.94	4	1.65	1.8
Sr	0.002	2.00	1	-	10.5
Ti	0.002	3.45	4	4.66	7.1
Tl	0.050	-	-	-	<
V	0.009	2.86	5	4.00	5.3
Zn	0.008	7.33	6	7.48	3.4
Zr	0.001	-	-	-	11.1

[1] Three times standard deviation of mean of calibration blank

[2] (measured concentration - accepted concentration) divided by accepted concentration

[3] RPD=Relative Percent Difference=(D1-D2/((D1+D2)/2))*100, where D1 and D2 are duplicates of same sample

* Range of duplicates less than 10 times detection limit

< Range of duplicates less than detection limit

Selected Analytic Procedural Examples: Chloride, Bromide, Iodide, Sulfate, Nitrogen (and Nitrate-Nitrite), Nitrogen (Ammonia), Carbon Dioxide. These are standard analytical procedures taken from ASTM Book of Standards except for Carbon Dioxide. The Carbon Dioxide reference is J. F. Dye, 1958.

ANALYSIS OF BRINES BY ASTM-EPA PROCEDURES

CHLORIDE

Method 325.3 (Titrimetric, Mercuric Nitrate)
STORET NO. 00940

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.
   1.3 Automated titration may be used.
2. Summary of Method
   2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
3. Comments
   3.1 Anions and cations at concentrations normally found in surface waters do not interfere. 3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H_2O_2.
4. Apparatus
   4.1 Standard laboratory titrimetric equipment including a 1 ml or 5 ml microburet with 0.01 ml graduations.
5. Reagents
   5.1 Standard sodium chloride, 0.025 N: Dissolve 1.4613 g ±0.0002 g sodium chloride (dried at 600 °C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark 1 ml = 886.5 μg Cl.
   5.2 Nitric acid, HNO_3 solution (3 + 997)
   5.3 Sodium hydroxide solution, NaOH, (10 g/l)
   5.4 Hydrogen peroxide (30%), H_2O_2
   5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric flask and dilute to the mark.
   5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g $Hg(NO_3)2{\cdot}H_20$ in 900 ml of distilled water acidified with 5.0 ml 45y conc. HNO_3 in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter, if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.
   5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)2{\cdot}H_20$ in 50 ml of distilled water acidified with 0.5 ml conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter, if necessary. Standardize against the standard
   5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2{\cdot}H_20$ in 25 ml of distilled water acidified with 0.25 ml of conc. HNO_3 (sp. gr. l .42) in a 1 liter

volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 μg of chloride.

5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100 ml volumetric flask and dilute to the mark with 95 % ethanol. Store in brown bottle and discard after 6 months.

5.10 Xylene cyanole FF solution: Dissolve 0.005 g of xylene cyanole FF dye in 95% ethanol or isopropanol in a 100 ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

6. Procedure

6.1 Use 50 ml of sample or an aliquot of sample diluted to 50 ml with distilled water, so that the concentration of chloride does not exceed 20 mg/50 ML. If the sample or aliquot contains more than 2.5 mg of chloride, use 0.025N mercuric nitrate titrant (5.7) in step 6.6. Determine an indicator blank, on 50 ml chloride-free water using step 6.6. If the sample contains less than 0.1 mg/l of chloride concentrate an appropriate volume to 50 ml.

6.2 Add 5 drops of mixed indicator reagent (5.9), shake or swirl solution.

6.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow

6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.

6.5 Add 1 ml excess HNO_3 solution (5.2).

6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Xylene cyanol FF solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

6.7 Additional steps to eliminate particular interferences:

6.7.1 If chromate is present and iron is not present the end point may be difficult to detect.

6.7.2 If chromate is present at > 100 mg/l and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).

6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).

6.7.4 If sulfite ion is present, add 0.5 ml of H_2O_2 solution (5.4) to 50 ml sample and mix for 1 minute.

7. Calculation

$$\text{mg chloride/l} = \frac{(A - B)N \times 35{,}453}{\text{ml of sample}}$$

where:
A = ml titrant for sample
B = ml titrant for blank
N = normality mercuric nitrate titrant

mg NaCl/l = mg chloride/l x 1.65

8. Precision and Accuracy
   8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	%	Accuracy as Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	~.51	~.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

   8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/l, the standard deviation was ±1.0.
   8.3 A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate-N, 0.25 mg/l nitrite-N, 259 mg/l sulfate and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D512-67, Method A, p 270 (1976).

BROMIDE

Method 320.1 (Titrimetric)
STORET NO. 71870

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial waste effluents.

1.2 The concentration range for this method is 2-20 mg bromide/l.

2. Summary of Method
   2.1 After pretreatment to remove interferences, the sample is divided into two aliquots. One aliquot is analyzed for iodide by converting the iodide to iodate with bromine water and titrating iodometrically with phenylarsine oxide (PAO) or sodium thiosulfate. The other aliquot is analyzed for iodide plus bromide by converting these halides to iodate and bromate with calcium hypochlorite and titrating iodometrically with PAO or sodium thiosulfate. Bromide is then calculated by difference.
3. Sample Handling and Preservation
   3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of oxidant and oxidant-quencher.
5. Reagents
   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered, colored bottle.
   5.3 Calcium Carbonate ($CaCO_3$): Powdered.
   5.4 Calcium Hypochlorite Solution ($Ca(OCl)_2$): Add 35 g of $Ca(OCl)_2$ to approximately 800 ml of distilled water in a 1 liter volumetric flask. Stir on a magnetic stirrer for approximately 30 minutes. Dilute to 1 liter and filter. Store in a glass-stoppered, colored flask
   5.5 Calcium Oxide (CaO): Anhydrous, powdered.
   5.6 Hydrochloric Acid Solution (1:4): Mix 100 ml of HCl (sp. gr. 1.19) with 400 ml of distilled water.
   5.7 Potassium Iodide (KI): Crystals, ACS Reagent Grade.
   5.8 Sodium Acetate Solution (275 g/l): Dissolve 275 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in distilled water. Dilute to 1 liter and filter.
   5.9 Sodium Chloride (NaCl): Crystals, ACS Reagent Grade.
   5.10 Sodium Formate Solution (500 g/l): Dissolve 50 g sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.
   5.11 Sodium Molybdate Solution (10 g/l): Dissolve 1 g sodium molybdate ($Na_2MoO_4 \cdot H_2O$) in distilled water and dilute to 100 ml.
   5.12 Sulfuric Acid Solution (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled -water.
   5.13 Phenylarsine Oxide (0.0375N): Hach Chemical Co., or equivalent. Standardize with 0.0375 N potassium biiodate (5.19, 5.23).

5.14 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Commercially available starch indicator such as thyodene or equivalent may be used.

5.16 Sodium Thiosulfate, Stock Solution, (0.75 N): Dissolve 186.14 g $Na_2S_2O3 \cdot H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

5.17 Sodium Thiosulfate Standard Titrant, (0.0375 N): Prepare by diluting 50.0 ml of stock solution (5.16) to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.19, 5.23).

5.18 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.17) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.19 Potassium Biiodate Standard, (0.0375 N): Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.20 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available dry, powdered starch indicators may be used in place of starch solution.

5.21 Nitrogen Gas: Cylinder

5.22 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.23 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N Sodium Thiosulfate: Dissolve approximately 2 g (±1.0 g) KI (5.7) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.12) followed by 20 ml standard potassium biiodate solution (5.19). Place in dark for 5 minutes, dilute to 300 ml and titrate with the phenylarsine oxide (5.13) or sodium thiosulfate (5.17) to a pale straw color. Add a small scoop of indicator (5.15). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.5) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodine Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to

approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.12).

6.2.2 Transfer the sample to a 250 ml widemouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask. A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.4.1).

6.2.3 Add 15 ml sodium acetate solution (5.8) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.10); mix well. Wait 5 minutes.

6.2.5 Purge space above sample with gentle stream of nitrogen (5.21) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5 g $KF{\cdot}2H_2O$ (5.22).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If the blank is consistently shown to be zero for a particular "lot" of chemicals, it can be ignored.

6.2.8 Titrate as described in 6.4.

6.3 Bromide Plus Iodide Determination

6.3.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, in a 150 ml beaker. Add 5 g NaCl and stir to dissolve. Neutralize by dropwise addition of HCl solution (5.6) as in (6.2.1). Transfer as in (6.2.2).

6.3.2 Add 20 ml of calcium hypochlorite solution (5.4). Add 1 ml of HCl solution (5.6) and add approximately 0.2 g calcium carbonate (5.3).

6.3.3 Heat to boiling on a hot plate; maintain boiling for 8 minutes.

6.3.4 Remove from hot plate and carefully add 4 ml sodium formate solution (5.10). Caution: TOO RAPID ADDITION MAY CAUSE FOAMING. Wash down sides with distilled water.

6.3.5 Return to hot plate and maintain boiling conditions for an additional 8 minutes. Occasionally wash down sides with distilled water if residue is deposited from boiling action.

6.3.6 Remove from hot plate. Wash down sides and allow to cool.

6.3.7 If a precipitate forms (iron), add 0.5 g $KF{\cdot}2H_2O$ (5.22).

6.3.8 Add 3 drops sodium molybdate solution (5.11).

6.3.9 A distilled water blank must be run with each set of samples because of iodide, iodate, bromide, and/or bromate in reagents.

6.3.10 Titrate as described in 6.4.

6.4 Titration

6.4.1 Dissolve approximately 1 g potassium iodide (5.7) in the sample from (6.2.8 or 6.3.10). Add 10 ml of H_2SO_4 solution (5.12) and place in the dark for 5 minutes.

6.4.2 Titrate with standardized phenylarsine oxide working standard (5.14) or sodium thiosulfate working standard (5.18), adding indicator (5.15 or 5.20) as the end point is approached (light straw color). Titrate to a colorless solution. Disregard the returning blue color.

7. Calculations

7.1 Principle: Iodide is determined by the titration of the sample as oxidized in (6.2): bromide plus iodide is determined by the titration of the sample as oxidized in (6.3). The amount of bromide is then determined by difference. Experimental data and a constant of 13,320 are entered in the appropriate places in equation (7.2) and the equation is solved for mg/l bromide.

7.2 Equation

$$Br(mg/l) = 13{,}320 \left[\left(\frac{A \times B}{C}\right) - \left(\frac{D \times E}{F}\right)\right]$$

where:

A = the number of ml of PAO needed to titrate the sample for bromide plus iodide (with the number of ml of PAO needed to titrate the blank subtracted).

B = the normality of the PAO needed to titrate the sample for bromide plus iodide.

C = the volume of sample taken (100 ml or a fraction thereof) to be titrated for bromide plus iodide.

D = the number of ml of PAO needed to titrate the sample for iodide (with the number of ml of PAO needed to titrate the blank subtracted). The blank for the iodide titration is often zero.

E = the normality of the PAO used to titrate the sample for iodide.

F = the volume of sample taken (100 ml or a fraction thereof) to be titrated for iodide.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 0.3, 2.8, 5.3, 10.3 and 20.3 mg/l of bromide, the standard deviations were ±0.13, ±0.37, ±0.38, ±0.44 and ±0.42mg/l, respectively.

8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 2.8, 5.3, 10.3 and 20.3 mg/l of bromide, recoveries were 96, 83, 97 and 99%, respectively.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1246-68, Method C, p. 328 (1976).
2. Bender, D. F., "Modification of the Iodimetric Titration Methods for the Determination of Bromide and its application to Mixed Domestic-Industrial Waste Effluents", Analyst (London), 100, p. 400-404 (June 1975).

IODIDE

Method 345.1 (Titrimetric)
STORET NO. 71865

1. Scope and Application
   1.1 This method is applicable to drinking, surface and saline waters, sewage and industrial waste effluents.
   1.2 The concentration range for this method is 2-20 mg/l of iodide.
2. Summary of Method
   2.1 After pretreatment to remove interferences, the sample is analyzed for iodide by converting the iodide to iodate with bromine water and titrating with phenylarsine oxide (PAO) or sodium thiosulfate.
3. Sample Handling and Preservation
   3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of bromine water and sodium formate solution instead of observing the light yellow color changes.
5. Reagents
   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered colored bottle.
   5.3 Calcium Oxide (CaO): Anhydrous, powdered.
   5.4 Potassium Iodide (KI): Crystals, ACS Reagent Grade.
   5.5 Sodium Acetate Solution (275 g/l): Dissolve 275 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot H_2O$) in distilled water. Dilute to 1 liter and filter.
   5.6 Sodium Formate Solution (500 g/l): Dissolve 50 g of sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.
   5.7 Nitrogen Gas: Cylinder.
   5.8 Sulfuric Acid Solution (1:4): Slowly add 200 ml of H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.
   5.9 Phenylarsine Oxide (0.0375 N): Hach Chemical Co. or equivalent. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).
   5.10 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.9) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.11 Commercially available starch indicators such as thyodene or equivalent may be used.

5.12 Sodium Thiosulfate, Stock Solution, 0.75 N: Dissolve 186.15 g ($Na_2S_2O_3 \cdot 5H_2O$) in boiled and cooled distilled water and dilute to 1.0 liter. Preserve by adding 5 ml chloroform.

5.13 Sodium Thiosulfate Standard Titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

5.14 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Potassium Biiodate Standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.16 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available, powdered starch indicators may be used in place of starch solution.

5.17 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.18 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (±1.0 g) KI (5.4) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.8) followed by 20 ml standard potassium biiodate solution (5.15). Place in the dark for 5 minutes, dilute to 300 ml and titrate with phenylarsine oxide (5.9) or sodium thiosulfate standard titrant (5.13) to a pale straw color. Add a small scoop of indicator (5.11). Wait until a homogeneous color develops and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.3) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodide Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.8).

6.2.2 Transfer the sample to a 250 ml wide-mouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask.

NOTE: A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.3.1).

6.2.3 Add 15 ml sodium acetate solution (5.5) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.6); mix well. Wait 5 minutes.

6.2.5 Purge the space above the sample with a gentle stream of nitrogen (5.7) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5g $KF{\cdot}2H_2O$(5.17).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If a blank is consistently shown to be zero for a particular "lot" of chemicals it can then be ignored.

6.3 Titration

6.3.1 Dissolve approximately 1 g potassium iodide (5.4) in sample. Add 10 ml of H_2SO_4 solution (5.8) and place in the dark for 5 minutes.

6.3.2 Titrate with phenylarsine oxide working standard (5.10) or sodium thiosulfate working standard solution (5.14) adding indicator (5.11 or 5.15) as the end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7. Calculations

$$I(mg/l) = 21{,}150 \left(\frac{ml \times N}{V}\right)$$

where:

ml = the number of ml of PAO needed to titrate the sample.

N = the normality of the PAO used to titrate the sample.

V = the volume of sample taken (100 ml or a fraction thereof)

21,150 was calculated from the number of equivalents of iodine produced when the potassium iodide was added and from the rearrangement of the equation to produce the value in terms of mg/l.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 1.6, 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, the standard deviations were ±0.23, ±0.17, +0.10, +0.06 and ±0.50mg/l, respectively.

8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent at concentrations of 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, recoveries were 80, 97, 97 and 92%, respectively.

Bibliography

1. Annual Book of ASTM Standards, Part 31",Water", Standard D1246-68, p. 328, Method C (1976).
2. Bender, D. F., "Modification of the Iodimetric Titration Method for the Determination of Bromide and its Application to Mixed Domestic-Industrial Waste Effluent", Analyst (London) 100, p. 400-404 (June 1975).

SULFATE

Method 375.4 (Turbidimetric)
STORET NO. Total 00945

1. Scope and Application
   - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/l.
   - 1.3 The minimum detectable limit is approximately 1 mg/l sulfate.
2. Summary of Method
   - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
   - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
   - 2.3 Silica in concentrations over 500 mg/l will interfere
3. Comments
   - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
   - 3.2 Preserve by refrigeration at 4°C.
4. Apparatus
   - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
   - 4.2 Photometer: one of the following which are given in order of preference.
     - 4.2.1 Nephelometer
     - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
     - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
   - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
   - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. Reagents

5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.

5.2 Barium chloride, $BaCl_2$, crystals, 20- to 30-mesh.

5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

5.4 Standard sulfate solution (1.00 ml = 100 μg SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3-5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter

B = ml Na_2CO_3 solution

C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 ml Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minute at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.
6.2.2 Measure turbidity at 30 second intervals for 4 minutes.
6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.
6.3.1 Prepare calibration curve using standard sulfate solution (5.4).
6.3.2 Space standards at 5 mg/l increments in the 0-40 mg/l sulfate range.
6.3.3 Above 50 mg/l the accuracy decreases and the suspensions lose stability.
6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

6.4 Correction for sample color and turbidity.
6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7. Calculations
7.1 Read mg $S0_4$ from calibration curve

$$mgSO_4/l = \frac{mg\ SO_4 \times 1{,}000}{ml\ sample}$$

8. Precision and Accuracy
8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Accuracy as Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.250 mg/l nitrite-N, 1.1 mg/l nitrate-N, and 42.5 mg/l total alkalinity (contributed by NaHCO3) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

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2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 496, Method 427C, (1975).

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)
STORET NO. Total 00630

1. Scope and Application
   1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter) and refrigeration. **Caution: Samples for reduction column must not be preserved with mercuric chloride.**
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45μm membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of the particulate matter present in the sample.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
   4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

5. Apparatus
   5.1 Reduction column: The column was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.
   5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.
6. Reagents
   6.1 Granulated cadmium: 40-60-mesh (MCB Reagents).
   6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:
      6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.
      6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.
      6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.
   6.3 Preparation of reduction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/l NO_3-N standard and 75 ml of ammonium chloride - EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.
   6.4 Ammonium chloride - EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.
   6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.
   6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)-ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.
   6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_20$ in distilled water and dilute to 1 liter.
   6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.
   6.9 Ammonium hydroxide, conc.
   6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.
   6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg NO_3-N.

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_3-N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO_2-N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_2-N.

6.16 Using a standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

Conc., mg-NO_3-N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45μm membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4-0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45μm membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7-10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. NOTE: If the concentration of sample exceeds 1.0 mg NO_3-N/l,

the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3-N mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mg } NO_2 + NO_3 - N/l = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg NO_3 + NO_2-N/l, the standard deviations were ±03.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg NO_3 + NO_2-N/l, the recoveries were 100%, 102% and 100%, respectively.

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3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p. 133-145.
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NITROGEN, AMMONIA

Method 350.3 (Potentiometric, Ion Selective Electrode)

STORET NO. Total 00610 Dissolved 00608

1. Scope and Application

1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.

1.2 This method covers the range from 0.03 to 1400 mg NH_3-N/l. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.

2. Summary of Method
   2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
   2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 Volatile amines act as a positive interference.
   4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
   5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
   5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
   5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
   6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
   6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).
   6.3 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).
   6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3-N. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask. NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350.1).
7. Procedure
   7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.
   7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the

solution until a stable reading is obtained. NOTE 2: The pH of the solution after the addition of NaOH must be above 11. Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3-N/l on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3-N/l.

8. Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3-N/l, standard deviations were ± 0.038, ± 0.017, ± 0.007, and ± 0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH_3-N/l, recoveries were 96% and 91%, respectively.

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Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Steam and Boiler Feed-Water with a Potentiometric Ammonia Probe", Analyst, 97 p. 626-633 (1972).

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Ilham Demir

Objectives/Purposes: Field determination of temperature, conductivity, Eh, and pH of produced fluids at the well site.
Collection of oil samples for subsequent oil chemistries.
Commercial lab analyses for selected anions and cations.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Field fluid sampling		Room 217	Oilgas	
Commercial lab tests			(Lotus 123)	

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As needed.

Analyses of Crude Oil Samples

Crude oil samples collected during the project from each field studied were logged into the Geochemistry Group's procedures. The reader is referred to the QA/QC and SOP plans for that group.

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Gary Salmon

Objectives/Purposes: Determine oil chemistries and certain HC ratios.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - ISGS Geochemistry Laboratories

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Oil Chemistry	(Note: see Geochemistry Group QA/QC procedure)			

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary.

PREPARATION OF THIN SECTIONS FOR MICROSCOPIC ANALYSIS

D. Scott Beaty

Scope and Use

This procedure covers the preparation of thin sections of clastic and carbonate rock samples for examination by transmitted light microscopy. This procedure yields no quantitative results.

Summary of the Procedure

Samples of oil well core as well as those of drill bit cuttings are prepared using similar methods. Core samples are cut to a specified size, depending upon sample availability, vacuum impregnated with epoxy, ground to the original rock surface by removing excess epoxy and then polished and mounted on a glass slide. Drill cuttings are placed into sample molds, vacuum impregnated with epoxy, ground to obtain a representative surface, polished and mounted on a glass slide. Both of the sample varieties are then cut and ground to 60 μm on a thin section machine (e.g. Microtec) and then ground from 60 μm down to 40 μm using a variable speed lapping wheel combined with a rotating sample holder (e.g. Struers). The last stage is one of hand grinding and polishing on a frosted glass plate to obtain a uniformly thin section approximately 30 μm thick. Finished thin sections are etched to record API# and depth, stained for carbonate minerals and then cover with a glass slip.

Caution- Epoxy should be handled using rubber gloves in a fume hood with good ventilation.

Equipment and Materials

1. Water-cooled saw with diamond-tipped blade--used to obtain small samples of a specific size from larger core samples and impregnated blocks.

2. Vacuum desiccator--used as a vacuum chamber to house samples during the vacuum impregnation process.

3. Vacuum pump--used to create a vacuum causing impregnation by epoxy and to displace air in porous and permeable rocks.

4. Aluminum molds--containers approximately 2 1/2 inches in diameter and 0.5 inch deep, which are used to hold core samples and epoxy during the vacuum impregnation procedure and while the sample hardens.

5. Plastic molds--containers which have four compartments, each of which is approximately 0.5 square in size. They are used to hold drill bit cuttings during the impregnation procedure and while the sample hardens.

6. Epoxy (Ring Chemical Company, 4-815-Resin) and hardening agent (Ring Chemical Company uersamid 140 Polyamid Resin for mounting and Ring Chemical Co. Geramid 250 Amidoamine resin for impregnation)--for impregnation and mounting samples. The epoxy should have a low enough viscosity to enter porous and permeable media when mixed in the correct proportions. It must have a high viscosity and good binding strength for gluing the prepared blocks and cutting molds to glass slides.

7. Frosted glass slides--27 x 46 mm are glued to polished and impregnated rock and cutting mold surfaces to allow light to be transmitted through the finished sample.

8. Keystone Oil Blue dye--mixed with the impregnation epoxy to highlight pores during microscopic examination.

9. Wooden tongue depressors--5 inch long tongue depressors are used for mixing the epoxy resin and hardening agent together and to apply binding epoxy to gluing surfaces.

10. Nalgene beakers--50 ml beakers are used during epoxy mixing and application processes.

11. Transmitted light microscope--used by the thin section maker for qualitative evaluations of section thickness, by use of interference colors. This is necessary in order to obtain a uniformly thick sample surface.

12. Grinding and polishing wheels--to grind off excess impregnation epoxy from sample surfaces and obtain a flat smooth surface for better adherence to a glass slide.

13. Grinding abrasives--240, 400, and 600-mesh silicon carbide grit are used to grind the rock surface, after excess epoxy is removed, as are 240, 320 and 600-mesh silicon carbide papers with adhesive backing.

14. Polishing compound--1000-mesh silicon carbide powder is used to polish the flat ground sample surface in preparation for its adherence to a frosted glass slide.

15. Lap wheels--rotating steel surfaces charged with grinding abrasives allow the thin section maker to obtain a uniformly flat surface.

16. Pressure sensitive grinding board--Water-washed metal surfaces upon which are mounted adhesive-backed silicon carbide grinding papers.

17. Microtec thin section machine to trim impregnated rock samples mounted on glass slides to a 120 μm thickness with a diamond-tipped saw blade and then grind them to 60 μm with a diamond impregnated grinding wheel.

18. Struers variable speed lap wheel with 5 place, weighted, rotating sample holder is used to lap the thin sections from 60 μm to 40 μm in thickness.

19. Beuhler-Ultramet III sonic cleaner--to remove grit between grinding phases.

20. Diamond tipped stylus--used to etch identifying codes on finished thin sections.

21. Carbonate stain--When dipped in Alizaren Red S and potassium ferricyanide stains, mixed in a 3:2 ratio, the researcher is able to distinguish carbonate minerals from non-carbonate minerals and more easily distinguish them from one another.

22. Cover slips--to maintain the proper free-working distance for the objective lenses during microscopic examination. these slips should be approximately 25 x 35 mm and be approximately 30 μm thick.

23. Canada Balsam, extra heavy mineral oil and water are all used to bind the cover slip to the thin section depending upon the types of analyses to be performed.

Sample Selection and Preparation

Sample Selection

Representative drill core and outcrop samples selected for thin section analysis are cut using a water-cooled, diamond-tipped rock saw to reduce them to a size small enough to be glued to a 27 x 46 mm glass slide. Representative drill cuttings are taken from preselected intervals.

Impregnation Procedure

Drill cuttings are placed in a 4 chambered plastic mold with an adhesive bottom which holds cutting chips at the bottom near a grinding surface. Each chamber will hold cuttings from a specific interval, therefore each mold could contain as many as four separate intervals.

Oriented blocks obtained from drill cores and outcrop samples are placed within aluminum molds which have been labelled with the proper API# and depth.

Epoxy resin and liquid hardening agent are mixed at a 2:1 ratio when used for impregnation and approximately 1 gram of Keystone Oil Blue dye per 100 ml of epoxy is added to highlight pore spaces during microscopic analysis. This mixture is poured into

the molds which are placed into a vacuum desiccator and subjected to a strong vacuum for approximately 1 hour. The molds are then removed and allowed to harden and cure for approximately 3 days.

Grinding Phase

The adhesive backing on drill cutting molds is removed and the impregnated sample is ground on lap wheels charged first with coarse 240-mesh and then with 400-mesh silicon carbide abrasive powder. Alternatively, the sample may be ground on a metal lap table to which 240 and 320-mesh silicon carbide adhesive backed papers are attached. In either case this step is done to remove excess epoxy from the impregnated sample and to expose a surface on the molded sample block which might be considered representative of the cutting interval.

Blocks from core and outcrop samples must be removed from their aluminum impregnation molds and the edges cut off with the rock saw to expose the outline of the original block and so that they will fit on a 27 x 46 mm frosted glass slide. The thin section maker must be careful at this point to mark the "up" orientation (direction toward the surface of the earth) if possible. Blocks are first ground on a 200 grit grinding wheel. The block is then ground on a grinding wheel charged with 240-mesh grit or on a metal thin section lap table covered with a 240 grit adhesive-backed silicon carbide paper to flatten and smooth the samples surface. The lap wheel is then charged with 400-mesh silicon carbide grit to further smooth the sample surface or a 320-mesh adhesive-backed silicon carbide grit paper is applied to the table to accomplish the same purpose.

At all stages of the grinding procedure it is important that the thin section maker be careful not to grind past the impregnated area of the sample on less porous and permeable blocks.

Final Grinding and Polishing Before Mounting of Samples

A final grinding stage is necessary to make the impregnated sample blocks and the impregnated cutting molds smooth enough to go on to a final polishing stage. Final grinding is accomplished by using 600-mesh silicon carbide powder on a lap wheel or 600-mesh silicon carbide adhesive-backed paper.

Final polishing is necessary to insure that the sample blocks adhere tightly to the surfaces of frosted glass slides. This stage is accomplished by the use of a frosted glass plate charged with 1000-mesh silicon carbide powder. Slight pressure is necessary to polish the sample to a smooth mirror finish.

Each grinding or polishing phase should be followed by a thorough cleaning of the sample to remove any grit which might still be present.

Mounting of Samples on Glass Slides

Mounting epoxy should be more viscous than impregnation epoxy so a more viscous hardening agent should be added to the mounting epoxy mixture. A 2:1 ratio of resin to hardening agent should be sufficient to bond the impregnated and polished thin section block to a frosted glass slide.

Glass slides are frosted by use of a diamond-impregnated grinding wheel on the Microtec thin section machine. Approximately 60 μm is removed from the surface of a precision glass slide to obtain a perfectly uniform thickness for all of the glass slides on the vacuum chuck. During the Microtec grinding slides should be returned to the same vacuum chuck to insure that all of the sections are ground to exactly the same thickness. Details of the slide frosting procedure are contained in the user manual supplied with the Microtec machine.

A few drops of the binding adhesive is applied to the face of the frosted glass slide and the sample surface and they are placed together. Slide and sample are then given slight pressure and are slowly rotated relative to one another to remove excess air from between them. Mounted samples are placed on a flat level surface and allowed to dry for several days.

Cutting and Grinding of Mounted Rock Samples

Samples are scraped with a razor blade to remove excess mounting epoxy which might have dripped onto the back of the slide during the mounting procedure. Epoxy buildups will affect the vacuum adhesion on the thin section machine and not allow the samples to be held tightly enough to the vacuum chuck. Seven samples, which were previously marked during glass slide frosting, are placed on the vacuum chuck in precisely the same orientation as they were placed during the slide frosting stage. This is necessary to insure accuracy during later grinding to 60 μm on the machine.

A diamond-tipped rock blade is mounted on the rotating spindle of the thin section machine. The vacuum chuck is then made to slowly rotate at a uniform speed into the fast-spinning blade which cuts the blocks at the proper thickness. The blade has been adjusted to insure that the section is trimmed to a uniform 120 μm thickness in addition to the thickness of the frosted glass slide.

A diamond-impregnated precision grinding wheel is mounted in place of the saw blade on the rotating spindle and the vacuum chuck is moved slowly into the fast-spinning wheel. This action causes the thin section to be ground 30 μm at a time to a 80 μm thickness and then two grinding steps are used to obtain a 60 μm thickness by removing 10 μm at a time. Two passes of the chuck past the grinding wheel must be made for each grinding phase to insure that a uniform thickness is maintained.

Details of the Microtec thin-sectioning process are contained in the manual supplied with the machine.

Final Grinding and Polishing of Thin Sections

The 60 μm thick sections are ground to 40 μm by using a variable speed Struers-Planopol (DP-U4) lap wheel combined with a rotating sample holder (PdM-Force). The lap wheel is charged with a slurry of glycerine and 600 grit silicon carbide grinding powder mixed in the following proportions:

280 ml glycerine
20 ml of distilled water
2 drops of dish washing liquid (to reduce surface tension)
4 heaping teaspoons of 600-mesh silicon carbide grit

After charging the lap wheel with a few splashes of the grinding slurry, sections are placed in the sample holders using two drops of glycerine as a temporary adhesive.. A splash of the slurry should be applied to the rotating lap every few minutes to keep it charged. Make sure the slurry is stirred well before each application. Samples should be lapped at the 75 RPM setting of the planopol with the sample holder (PdM force) rotating. Grinding time varies from sample to sample. In general, siliclastic samples should be checked every minute depending on surface area and carbonates should be checked every 45 seconds. It is possible for a carbonate thin section to be finished in as little as 45 seconds so it is imperative that they be checked frequently.

For siliciclastic core samples and well cutting samples, grinding times are dependent on the amount of impregnation epoxy which they contain. Those which contain the most epoxy will take the longest to grind.

Experimentation is necessary for each sample set, but the following rules of thumb might be helpful:

Siliclastics and well cutting samples take 1.5 to 15 minutes.
Sandstone, no epoxy (low ⌀) - 1.5 to 3 minutes
Highly porous no epoxy rim - 3.5 to 7 minutes
Highly porous with epoxy rim - 5 to 10 minutes
No porosity with epoxy rim - 3 to 7 minutes

Well cuttings always contain epoxy between sample chips and take longer to grind.
SS - 7 to 15 minutes
LS - 5 to 12 minutes

Limestone

Low ⌀ (no epoxy) - 45 seconds to 2.5 minutes
High ⌀ (highly impregnated) - 1.5 to 4 minutes
With epoxy rim - add 45 seconds to 1.5 minutes

The 40-μm thick sections must be ground on 600-mesh silicon carbide adhesive-backed paper mounted on a water-washed thin section lapping table. Sections are then ground on a frosted glass plate charged with 1000-mesh silicon carbide powder, checking frequently under a transmitted light microscope to insure that the section is of a uniform thickness. This is accomplished by making sure that individual mineral grains show the correct interference colors which are so crucial to microscopic evaluation. The thin sections are thoroughly cleaned after each grinding step using an ultra sonic cleaner to ensure that no grit is present to adulterate the finer grained powder or polish.

The backs of finished samples are etched with a diamond tipped stylus to document both API# and depth.

Thin sections are then stained using Alizarin Red S and potassium ferricyanide carbonate stains to highlight the different carbonate minerals thus distinguishing them from non-carbonate minerals and from one another. Thin sections are dipped in a 3:2 Aliziran Red S to potassium ferricyanide solution for approximately 1 minute, washed under running distilled water to remove excess stain and are then allowed to air dry.

The thin sections are stored in a box provided for this purpose and delivered to the petrographer for subsequent analysis.

Prior to analysis, thin sections are covered with glass slips by using mineral oil and water.

Grinding and polishing laps and other work areas are cleaned and supplies are stored in designated cabinets.

Section Polishing for SEM/EDX Examination

After completion, thin sections may be polished to a very high gloss by wet or dry grinding with 5-, 1-, 0.3- and 0.05-μm micropolish. To accomplish this, wet slurries of the micropolish are added to the variable speed Struers-Planopol (DP-U4) lap wheel with a silk polishing cloth on the surface. Slurries should contain 1 level teaspoon of micropolish powder and 2 teaspoons of water.

1. Add slurry of 5μm micropolish to lap surface.
2. Move the rotating sample holder to the surface and make sure the sample will stay on the charged silk polishing cloth.
3. Turn on the DP-U4 and set speed at 25 to 50 RPM. Turn on the sample holder.

4. Polish from 0.5 to 3 minutes, while wetting the surface of the lap wheel with a squirt bottle (a very small amount of water) every 15 seconds.
5. Change the silk cloth (retaining it for future use and marking it to show the size of polish used). Wash the lap wheel very carefully.
6. Go to next smaller polish size (1 micron) and repeat steps 1 through 5.
7. The last step will be the 0.05 micron polishing medium.

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: D. Scott Beaty

Objectives/Purposes: Preparation of thin sections.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 31 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
NA	NA	NA	NA	NA

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - NA

Changes - As necessary

COMPLETION AND STORAGE OF SAMPLES: THIN SECTION, SEM AND X-RAY LAB

D. Scott Beaty

Thin sections are made according to guidelines established by the standard operating procedure. Sections are stored in cabinets intended to house specimens generated by the DOE/IOR project in Room 100A, Illinois State Geological Survey.

Samples for quantitative x-ray mineral analysis are taken adjacent to the block cut for thin section analysis. Samples are taken at the time of cutting to insure that a representative fraction is analyzed. Samples are prepared using a modification of the standard operating procedure. During clay separation procedures bleach is added as an intermediate step before acidifying the sample. The remainder of sample (unaltered) is kept in Room 100, Natural Resources Building.

Samples taken for Scanning Electron Microscopy (SEM) are prepared according to methods outlined in the standard operating procedure. Samples are taken in close proximity to samples taken for thin section and x-ray analysis. These samples will not be saved because they hydrate readily.

A computer listing of samples produced in the project is being compiled, making them available for future reference. The list will be generated from standard request forms that document location and sample type for each sample.

A master sample list is kept in the files of the Oil and Gas Section in Rm.102, Natural Resources Building. This is a more complete inventory of analyses and includes the well name, API number, depth, field (or location from outcrop), formation, and a Clay Minerals Unit petrographic number. The various types of analyses performed on each sample are also included. These analyses include: thin section analysis, x-ray bulk and clay mineral analysis, x-ray analysis of chlorite Fe:Mg, and others which are enumerated and described separately.

Photographs of thin sections are handled by the investigator in charge of the corresponding field study, as are SEM photos.

ENGINEERING LAB SAMPLING PROCEDURES

When sampling for crude oil, oilfield brine or gas, the person collecting the sample will ensure that proper steps are taken to obtain an uncontaminated sample from the zone of interest. Wells being treated with additives(corrosion inhibitors, paraffin remover, scale inhibitor, etc.) should be avoided when possible, otherwise treatment should be discontinued at least 24 hours prior to sampling.

In coring, cutting or saturating the plugs, care should be taken to maintain the original state of the core. Produced brine from the formation or synthetic brine prepared in the laboratory will be used as the cutting or saturating fluid for the plugs.

Sample Storage

Immediately after sampling, proper labels are attached to all containers clearly identifying the contents, how the sample was taken, the date, the location, and the name of the sampler. Brine will be sealed and stored in plastic bottles and oil in capped, metal cans under the vacuum oven table. After the core plugs have been analyzed, they are wrapped in cellophane and systematically stored in the plug cabinet. All of the above are in Room 33, Illinois State Geological Survey. Core samples received from the operator are housed at the ISGS Annex and indexed by Annex personnel.

Sample Identification

Core samples are identified by field, well, and depth interval. Marked clearly on each plug, after it is cut, is an identification code and arrow. The code is a type of subscript used to fully identify the plug and experiment, and the arrow designates flow direction.

Sampling Purpose

Plans for the sample are noted beforehand to insure that only necessary procedures are used and necessary samples are obtained. This eliminates waste and saves space.

Analytical Procedures

Analytical procedures are described in written Standard Operating Procedure (SOP) manuals for each analysis. Presently, SOP manuals are complete for the Helium Porosimeter, Gas Permeameter and the Core Flooding system.

Calibration Procedure and Frequency

Instruments used for quantitative rock property measurements and flow tests are calibrated as often as necessary to maintain the maximum accuracy. Records of calibration are kept in a notebook reporting the date, which apparatus is being calibrated, the calibrating device, and the person conducting the calibration. Detailed procedures are described in the SOP manuals.

Method Validation

Analytical methods are validated by comparison to optional methods (for example, porosity by the gas expansion method versus porosity by the total saturation method), results on the same samples by another lab, and by using standards of known results.

Data Reduction and Reporting

As data are generated and reduced, the results are monitored to eliminate obvious errors. In-lab computer software reduces the raw data to the desired final product. Currently stored on floppy discs, are the programs Poros, Permg and PVKL which calculate porosity, gas permeability and liquid permeability from the raw data generated by the Helium Porosimeter, the Gas Permeameter, and the Core Flow Unit. The software programs for each instrument also include the calculation of the mean value and standard deviation for statistical analysis. After the data are thoroughly scrutinized for precision and accuracy, the report is written in a general format or one previously established by the requestor.

Documentation

Bound laboratory notebooks are used to document all raw data, observations, calibrations and any other pertinent information. Computer programs containing data storage, retrieval, calculations, and plots are user friendly to ensure understanding by even those not familiar with the lab. A standard summary report form summarizes the calculated values prior to the analysis of the results. Rough data sheets, operating procedure manuals, reports completed and all other important papers are kept on file. These files and the computer discs mentioned above are located in a filing cabinet in Rm.33, Natural Resources Building.

Preventive Maintenance and Repair

Each manufacturer's preventive maintenance schedule is followed for each piece of equipment. The laboratory personnel responsible for this maintenance must document each task completed and should record any time-saving hints and problem solutions.

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: D. Scott Beaty

Objectives/Purposes: Sample storage

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 33 and 100A of the Natural Resources Building, Illinois State Geological Survey.

Data Records - See SOP

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
Sample storage		Room 200	Beaty	

Initial publication plan: NA

Planned schedule of project reviews: NA

Reports - NA

Changes - As necessary

RESERVOIR CHARACTERIZATION USING SEM/EDS

Beverly Seyler

Scope and Use

This methodology provides a semi-quantitative elemental analysis of reservoir rock samples. The scanning electron microscope (SEM)/energy-dispersive spectrometry (EDS) is used for a high resolution, three dimensional view of samples. The SEM/EDS system permits both viewing and elemental analysis of grains, pores, and pore-lining minerals that comprise reservoirs. This aids in the petrographic evaluation of reservoirs and is an integral part of reservoir characterization and the determination of that portion of a reservoir that will come into contact with drilling, completion, and recovery fluids. Conclusions based on this method are best made when complemented by thin section and XRD analyses.

This procedure is based on the capabilities of a scanning electron microscope equipped with an energy dispersive x-ray analyzer (SEM/EDS). The inherent resolution of the SEM/EDS instrument enables the direct determination of an elemental spectrum for areas as small as 1 micrometer in diameter within a sample.

The analyst is required to identify pore minerals, clay minerals, and framework grains in sedimentary rocks. Therefore, completion of a university-level course in mineralogy and sedimentary petrography or equivalent training is prerequisite to identifying necessary components. Additional training in the form of university-level courses in the theory and operation of scanning electron microscopes and microbeam analysis is also prerequisite to operation of the SEM/EDS. After prerequisite training, an additional 2 to 4 weeks of training, specifically on the Amray 1830 SEM and Noran microbeam analysis system, is necessary.

General Principals

Reservoir samples are first analyzed by XRD and/or thin section methods to determine bulk mineralogy, general composition of framework grains, and clay mineralogy.

The SEM/EDX method is based on collecting and processing characteristic x-rays generated by interaction of a high-energy electron beam with atoms in a sample. The incident high-energy electrons excite the atoms to a higher energy state at and under the spot in the sample where the beam strikes. X-rays characteristic of the elements present at the spot are emitted as the excited atoms return to their stable ground state. The characteristic x-ray peak intensity is proportional to the concentration of that element in the sample. Detection of elements of atomic weights 11 (Sodium, Na) or greater is possible using a LiSi crystal and beryllium window. Recently, a new diamond window detector capable of detecting elements with atomic weight of 6 (Carbon) or greater was

purchased. After installation of the new detector, samples were coated with Au/Pd for greater visual resolution.

Relative weight percentages of detected elements are compared with formulas of minerals known to occur as determined by XRD or thin section analyses. Coupled with crystal form, habit, etc., this permits identification of minerals. Relative amounts of Fe, Mg, K, and other detected elements are also determined for pore lining minerals, in particular, authigenic clays. The Fe content is particularly important due to potential adverse reactions with drilling, completion and recovery fluids.

The development of standards for specific clay minerals is an ongoing process. These will be incorporated and used for comparisons as suitable standards are found during the course of this study.

Equipment and Supplies

Scanning Electron Microscope (SEM), Amray Model 1830, equipped with an energy dispersive X-ray Analyzer (Noran, Model 5500, Series II).

Sputter coater and carbon module, a vacuum coater for coating SEM specimens.

Instant film, Polaroid type 55 P/N for SEM documentation.

Desiccator cabinet for storage of prepared samples.

Procedure

Specific operating instructions on the SEM, the EDX, and the sputter coater for doing these evaluations are given in the detailed instructions filed in the SEM laboratory.

Where possible, samples are glued to SEM stubs using colloidal graphite or silver conductive paint as the gluing medium. Samples are placed in the vacuum chamber of the carbon sputter coater or Au/Pd for a minimum of 30 minutes. A high vacuum and sputter action serve to outgas hydrocarbons in the sample.

X-ray spectra are obtained for samples using the spot, partial field or full screen mode of SEM operation. The following operating parameters for the SEM are optimal for most samples: acceleration voltage of 15 kV, condenser lens setting of ~4.0, working distance of 20 mm, specimen tilt of 0°, take-off angle of 35.6°, and LaBb filament. The condenser lens setting is varied to obtain appropriate deadtime of 20%.

The above operating conditions yield a count rate for EDX of about 1000-3000 cps for regular specimens in the partial field mode. Under these operating conditions the minimum count rate for the sample should be 1000 or above in order to obtain

Project Plan and Review - QA/QC

Project title: DOE/ENR: Improved Enhanced Oil Recovery in Illinois through Reservoir Characterization

ISGS Program: Oil and Gas

Project Leader: Donald F. Oltz

Other Investigators: Beverly Seyler

Objectives/Purposes: High resolution examination of reservoir pores. Semi-quantitative elemental analyses.

Project tasks and planned start/end dates: As needed over project life

Procedures for Data Compilation - As given in attached SOP

Facilities - Work is carried out in room 17 of the Natural Resources Building, Illinois State Geological Survey.

Data Records -

		File storage locations		
Task #	Record (brief title)	Hard copy	Disk & directory	Computer
SEM/XRD	Catalog, Room 100	Photograph Graph	Diskette	EDX System

Initial publication plan:

Planned schedule of project reviews: As needed. Coordination meetings are held weekly; formal reviews at six-month intervals.

Reports - Data generated are used in field studies published as part of the Illinois Petroleum series. Data are also used in engineering models.

Changes - As necessary

reasonable results. Adjustment of the condenser lens is sometimes needed to achieve this count rate.

A counting time of either 30 or 60 seconds was found to be satisfactory for collecting x-ray signals from sample spots impacted by an electron beam of approximately 100 A diameter or a partial field of $(10mm)^2$.

Photomicrographs and spectral analyses using the SQ program by Noran are used to record minerals, clay minerals, pore-minerals, and other associated elemental analyses.

X-ray maps of polished samples were made where quantitative analyses were most important.

The particle measuring mode on the SEM is used to measure pore size, grain size, etc., for each sample.

CLAY MINERALS

R. E. Hughes

Scope and Use of Methods

These methods are used for the mineralogical analysis of the oil reservoir sandstones of Illinois. The methods also have been applied without modification to clay partings, shales, and limestones associated with the sandstones. The methods have undergone periodic modifications to attempt to improve accuracy and precision. However, the sample set has been revised so that the results from all field studies are comparable. Replicates are to be run whenever possible. The goal is to replicate 10-15% of each sample set. Generally, a bulk pack, <16μm smear, and optional <2μm or finer samples should all be replicated on the same sample.

General Principles and Summary of Methods:

See general x-ray diffraction (XRD) SOPs attached.

CAUTION: THE U.S. EPA HAS RECENTLY CLASSIFIED ALL MATERIALS CONTAINING MORE THAN 0.1% CRYSTALLINE SILICA AS A PROBABLE RESPIRATORY *CARCINOGEN*, AND YOU SHOULD OBTAIN MATERIAL SAFETY DATA SHEETS ON SAFE HANDLING. ALL POWDERS SHOULD BE HANDLED IN A FUME HOOD AND SOMETIMES WEARING A RESPIRATOR IS REQUIRED.

Method A. Random Powder Pack (See general instructions below).

Current procedures for powder packs are to use up to 4 grams of bulk sample; add 7.0% KCl internal standard (used 5% until 7/91); place bulk sample with standard in dry or propanol-rinsed McCrone® micronizer cup w/elements + ~10 ml KCl-saturated propanol; grind 6 min; wash sample into 50 ml centrifuge tube and centrifuge @2000 RPM for 10-20 min; pour off clear propanol (may save for later use); dry sample in tube at ~70°C. **In fume hood**, mix dry powder in tube, fill side-loading holder (see SOPs and appendixes below); analyze with Scintag® XRD spectrometer (40KV, 30MA, 1°2Θ/min, .03 chopper, 4° to 34°2Θ); obtain peak areas by "deconvolution" program; calculate by standard ratios (Qtz1:Qtz2 = 0.183; Qtz1:K-feld or plag = 0.391; Qtz1:calcite = 0.21; Qtz1:dolomite = 0.23; Qtz1:pyrite = 0.45); Note at the time of this writing, we also were estimating clay content as = 2 X 020 peak area/2 X 020 peak area + corrected Σnon-clay intensities); see below for reports of results.

Comments: If any containers such as cups and tubes are washed in water, it is important that they be dried or rinsed in propanol before KCl-containing samples are added. Operation of the lab instruments is fully described in the general SOP-QA/QC plans.

A recent (2/92) addition to this method involves weighing the dried sample for Method B below, before and after treatment with acetic acid. The weight percent calcite + dolomite determined in this way correlates with an ***r*** of 0.997 with carbonate percentages determined by the XRD-KCl addition method. If enough sample is available, it also is valuable to obtain a loss-on-ignition (LOI) determination of the bulk acetic acid-residue sample. (When the amount of sample is small, the micronized powder from Method B can be used for %carbonate and %LOI determinations. The LOI can be compared with the "expected" percentage of hydroxyl water loss from the XRD analysis, and refinements can be made in quantitative estimates of the mineral content. Note that the best LOI temperature range for this purpose is 300°-1000°C; heating from 100°C to 1000°C, the normal procedure, will give excessively high LOIs due to inclusion of interlayer water from clay minerals. (Further note that diagenetic illite and I/S contain hydronium and water molecules substituted for K^+ in the interlayer, and these substituted molecules will be included in the LOI.)

Method B. <16μm Size-Fraction Smear

Up to 4 g of bulk sample is used. A mixture of 100 ml of laundry bleach ("Chlorox" NaOCl) is made with 200 ml H_2O; the mixture is added to 4 g of sample (150 ml to 2 g, etc.) and the sample is heated to near boiling on a hot plate in the hood. The mixture is stirred and allowed to react overnight; the clear bleach solution is decanted and a mixture of 100 ml of glacial acetic acid to 200 ml H_2O is added (always add acid to water), again on a 300 ml-to-4 g basis, stirred, and allowed to react overnight. The clear acid solution is decanted, the samples are transferred to plastic beakers for 30 sec ultrasonic dispersion at 60% full power, washed through a 325-mesh screen, and 400 ml H_2O washes are repeated twice, or until the fine fraction begins to disperse. A few drops of standard dispersant solution A (solution "A": 200 g/l Calgon and 50 g/l Na_2CO_3) is added to the partly dispersed samples and the samples are stirred, settled 0.75 min per cm of slurry depth, and poured into a 600 ml beaker. The settling step is repeated twice and the combined clay-silt fraction is flocculated with 1:1 HCl solution and allowed to settle. The clear supernate is decanted and the <16μm samples are transferred to 50 ml centrifuge tubes and centrifuged for 10-20 min at ~2000 RPM. The clear supernate is poured off, the plugs or pastes are stirred with a microspatula, and the pastes are smeared on a round disk with the microspatula for XRD analysis (see general SOPs). After at least 2 days solvation with ethylene glycol at 28°C, the samples are scanned from 3 to 34°2Θ at 2°2Θ/min (0.03 chopper). The samples are re-scanned after heating for at least 1 hr at 300-350°C (as close to one hour as possible). Peak areas are collected by the Scintag® deconvolution methods, and results are calculated using reference intensity ratios (RIRs) of illite001 = 1.0; collapsed I/S001 and smectite001 = 1.0; glycol solvated smectite001 = 6.0; kaolinite001 and chlorite2 = 0.40.

Comments: Generally, the percentages of clay minerals are reported in whole number percentages on a 100% basis. The decimal fractions are carried along in the spreadsheet and reported as absolute percentages on a bulk-sample basis. Samples with

little clay often are difficult to settle because the coarse fraction mixes during pour-off. The solution to this problem is to screen out the >325-mesh (44μm) fraction and be as careful as possible during settling. The quartz- and feldspar-to-clay-mineral ratio of the smears also can be used to estimate carbonate-free clay-to-nonclay mineral contents. These estimates can be compared to results using the 020 peak of the bulk pack and the absolute nonclay contents determined by internal standards. (Note discussion under Method A above about the value of obtaining an LOI on the acid residue of a bulk sample.)

Method C. <2μm and finer Sedimented Slides

See general SOP for these methods. At present, we use the Scintag® deconvolution program for measuring the areas, heights, and widths of all peaks from the XRD traces of these samples. D. M. Moore has developed a method for determination of the amount of S/C interlayering in chlorite (see D below).

Method D. Measuring Peak Widths of Chlorites Suspected of Having 7Å Interlayered Material

The <2μm fraction is prepared as an oriented aggregate (see Method 4 for this procedure). X-ray diffraction tracings, using CuK_α radiation, are digitally recorded, most commonly from 2 to 33°2Θ at 1°2Θ/minute. The widths of the first five orders of the 00*l* series of peaks are separately displayed on a terminal screen so that the top of the peak is at the top of the screen, its base above background is at the bottom of the screen, and the horizontal scale is 3°2Θ across the full screen width. The width of the peak is then measured in °2Θ at one half of the peak height. For cases in which there is enough interference to distort or overlap the 003 peak position of chlorite by the 002 peak of illite or at the 004 peak position of chlorite by the 002 peak of kaolinite, one-half of the peak width at half maximum on the side away from the interference is measured and then doubled (Moore and Reynolds, 1989). To measure the precision of this method, three slides made from the same suspension were each run five times. The ratio of the width at half-maximum of the 003 peak divided by that of the 004 peak as a measure of peak broadening was 1.34 with a first standard deviation of ±0.06 or about 4.5%. These measurements had no corrections for instrumental signature or angle-dependent particle size effect.

XRD LAB

R. E. Hughes

The choice of a method of X-ray diffraction (XRD) analysis usually depends on the problem at hand. Four methods are outlined below; however, certain problems require a modification of prior methods or creation of a new approach. For example, a thesis problem of a few years ago in the northeastern U.S. required an assessment of hydrobiotite content. Lacking a standard for this mineral, we assigned a factor to the mineral and cautioned the student to present his results as relative differences.

Scope and Use of Methods

The methods described herein are used to determine the mineral content–principally clay mineral content–of earth materials. The methods have been used extensively on Quaternary materials and on clastics associated with coals in the Pennsylvanian strata of Illinois. They have been applied to modern and ancient soils; the clay fraction of tills and related diamictons; the fine fraction of outwash and lacustrine silts, sands, and gravels; the low-temperature (LTA) mineral matter and bulk samples of coal and related organic-rich materials; the fine fractions and bulk samples of the range of clastic and carbonate rocks found in Illinois; the acetic acid or hydrochloric acid residues of limestones, dolomites, and siderite concretions; the magnetic or heavy liquid separates of several geological materials; and the combustion and conversion products of Illinois coals. A significant number of inorganic compounds are identified and quantitatively estimated in our laboratory every year. The methods are used to determine relative or approximate amounts, i.e., greater or lesser amounts of a mineral in a particular type of material, rather than absolute determinations. However, for some projects, accurate quantitative estimates are attempted.

General Principles and Summary of Methods:

The methods employ the intensity of selected X-ray diffraction (XRD) peaks from an XRD trace to quantify mineral content. Good general references for XRD analysis are given in the references.

The accuracy of XRD analyses is known to vary as a function of the composition of the material studied. Fairly high precisions are possible, but, whenever possible the results should always be reported as relative differences. Comparisons of quantitative estimates of different types of material should only be attempted with caution, and several qualifiers including reasons for the assumed validity of the comparison should be stated. On the whole, the analyses give consistent results, particularly with materials that have been analyzed many times before. The results should not be referred to as "semi-quantitative"; they are quantitative with precisions that can be determined and with variable accuracies. D. M. Moore has recently suggested "quantitative representation" (QR) as a term for sample analyses where precision is measured but accuracy is

unknown. By contrast "quantitative analysis" (QA) can be reserved for cases where both precision and accuracy are determined.

There are four ways in which standards are used in XRD: 1) internal standards are minerals or compounds not present in the unknown sample that are added in known amounts of the sample; 2) external standards are those in which the peak intensity of a phase is determined and that value is used to quantify the same mineral in an unknown; 3) additive standards are those in which a mineral in the unknown sample, such as quartz, is added in known amounts to calculate the content before additions. The known phase can then be used as an internal standard; 4) calculated standards are a special case of external standards in which the intensity of a peak for a pure phase is calculated from the structure factor of the mineral. We are rapidly moving in the direction of nonclay determination with internal standards (corundum, dolomite, fluorite, KCl, Li_2CO_3) and clay mineral determinations by comparison with calculated standards (see discussion of NEWMOD® under precision and accuracy).

Precision and Accuracy

The replicate analyses carried out for all sample sets allow a calculation of precision. The first check of precision indicated that the relative percentage calculations had fairly high precisions, <5-10% of the amount estimated. However, the clay content calculation based on the 020 clay peak method on the bulk pack **or** the internal standard method gave large errors. Because no standards exist for these types of samples, it is impossible to measure accuracy in an exact way for this project. About the only way to approach the problem is to make up some standards from well known occurrences of the minerals that are common in these samples —quartz, both feldspars, calcite, dolomite, illite, I/S, kaolinite, various forms of chlorite, and smectite (from drilling mud). If some recent improvements in our internal standard methods solve some past problems, it will be possible to assemble a small set of "standards" in the near future, and, by repeating the analysis of these samples from time to time, to report the equivalent of accuracy from a chemical analysis. Until the last of these problems has been solved, accuracy will remain uncertain. It may be possible to obtain chemical analyses of a small number of samples that represent extremes in apparent mineral content. The chemical results could then be used to estimate accuracy, but the results are always distorted by solid solution within clay and nonclay minerals.

A method is under development that could solve many of these problems. This method makes use of the relationships derived from NEWMOD® to calculate the varieties and then relative amounts of each of the clay minerals. Because the internal standard method works reliably, the relative clay percentages can be multiplied by clay mineral content determined from the bulk pack to give a reliable absolute analysis of all the minerals in geological samples. Of course these methods were primarily developed for reservoir sandstones, and occasional clays, shales, and limestones or dolomites cannot be expected to give as high an accuracy. Samples with abundant kaolinite are not as well

sampled by our <16μm smear methods (kaolinite often occurs in vermicules up to 100μm in size). To sum up, these results are probably good to about ±10% of the amount determined, especially for the major constituent(s) such as quartz, calcite, or dolomite. When a mineral is present in small amounts, the error can easily exceed 50%.

These methods are based on the best approximation of the diffraction effects from "standard" minerals available at the ISGS over the past several decades. Standard minerals: quartz from St. Peter Sandstone near Ottawa, Illinois; illite from near Fithian, Illinois; kaolinite from Georgia or from the waste slimes of St. Peter Sandstone mining in north central Illinois; chlorite from Chester County, Pennsylvania; smectite from Mississippi and Wyoming; dolomite from Thorton Quarry in Cook County, Illinois; calcite from near St Genevieve, Missouri. It is increasingly common to use computer-calculated intensities for external standards. The Clay Unit currently has NEWMOD®, a program by R. C. Reynolds, Jr. that calculates peak intensities for most of the clay minerals with reference to quartz as a standard reference intensity. Similar programs for the random patterns of nonclay minerals are available from Dean Smith at Penn State University.

The new standard for the ISGS for replicate analyses suggested by R. A. Griffin is a minimum of 10-15%. Actually, chemists typically use 5% blank analyses and 10% replicates. However, although it is a good idea to run an XRD trace of the glass slides, cover slips, disks, and sample holders used to recognize "show through" when it occurs, blank analyses have little value in XRD. In cases where high precision and/or accuracy are required, it may be necessary to run more replicates.

Method 1. Random Powder Pack

A. Uses of Method:

This method is used for identification of unknown minerals and chemicals, estimation of mineral content and of clay mineral to nonclay mineral ratios, and determination of crystallite size and clay mineral polytypes. The detection limits for minerals vary from about 0.5% to 10% or more. We prefer to match the d spacings and approximate intensities of at least 3 major peaks for the identification of an unknown phase. However, an identification and quantitative estimation can be made on one or two peaks when they are common ones and the phase is "expected" in the sample.

Detection limits of a single mineral depend on the effects of associated phases, on the peak intensity of the most intense peak(s) of the phase of interest, and on the degree to which diagnostic peaks are overlapped by peaks of other minerals. For example, the detection of quartz in kaolinite becomes difficult at about 0.5-1.0 % due to overlap of a weak kaolinite peak with the most intense peak for quartz.

This method has been applied to a wide range of geological materials including claystones, sandstones, siltstones, coals (and LTA of coals), limestones, soils, etc.

B. Equipment required:

Currently available XRD instruments: One General Electric® (GE) XRD-5 diffractometer (circa 1952) with a Ni K_β filter; one Philips/Norelco® diffractometer (circa 1968) with a scintillation detector and a graphite monochromator; and one Scintag® ⊖/⊖ goniometer (circa 1986), a liquid N_2-cooled germanium detector, and a 12-position automatic sample changer. Equipment required for sample preparation: A medium size mortar (~100 ml) and pestle (porcelain, mullite, or agate), a micropulveriser, or grinder such as the McCrone® Micronizer; sample holders, preferably side-loading type; fill funnel or weighing paper (4X4"); large paper clips for holding cover slide to sample holder; 27x46 mm glass slides for holder covers; propanol for micronizing soluble phases; and 25 mm round glass disks and an eye dropper for slurry mounts.

C. Sample Preparation

1. Samples should be ground by hand with a mortar and pestle or micropulverizer until all grains are reduced to <0.5 mm. Care should be taken not to over grind the sample, because the structure of minerals will be destroyed after excessive grinding. If high levels of precision and accuracy are required, a sequence of repetitive grinding and XRD sample analysis may be necessary. The pulverized sample is then ground with a McCrone Micronizer® in water or propanol. For most materials, 5-10 min grinding gives a powder with 5-10μm as the dominant size. Current procedures for powder packs are to use up to 4 grams of bulk sample; add an internal standard if desired; place bulk sample with standard in a McCrone® micronizer cup w/elements + ~10 ml H_2O or propanol; grind 6-10 min; wash sample into 50 ml centrifuge tube and centrifuge @2000 RPM for 10-20 min; pour off clear supernate; dry sample in tube at ~70°C. **In fume hood**, mix dry powder in mortar, fill side-loading holder for XRD analysis.

2. Samples should be placed in side-loading sample holders whenever possible. Holders are filled by clamping a glass slide to the holder as a cover and pouring the sample through a funnel or folded piece of weighing paper. Side loaders should be filled three times after settling the powder with a tap or two, and/or compressing it with a fitted tongue depressor (plunger). With micronized samples, it is necessary to use some sort of plunger to compress the powder in the holder. We have found that micronized samples are ground well enough that smears and various types of powder-mounting methods give similar results for all but the most anisotropic minerals. With small samples, it may be necessary to employ front-loading powder holders or deposition of a slurry of the powder on a glass slide. If perfect random orientation of fine-grained materials such as clays is the goal of the analysis, samples can be spray dried and packed in side-loading holders (see Reference IV). High-absorbance minerals such as pyrite must be ground to ~<2μm. If accuracy is a goal, it is necessary to add a known amount of a standard mineral/compound such as corundum, dolomite, fluorite, sylvite, or Li_2CO_3, or chemically determine the amount of one or more of the minerals in the sample and use that value as an internal standard (see method A for EOR/DOE).

D. XRD Analysis

The operating manuals for the diffractometers are located near the XRD units in Rooms 319 and 321. In general, one must be sure the cooling radiator on the GE is full of demineralized water; the cooling unit for the Philips and Scintag is operating and the coolant level is about 65°F; the GE switch is turned to Line first and then X-ray; the Philips and Scintag switches should be turned to KV first, to operating level (usually 40 KV), and then MA to operating level (~20-30 MA). KV, MA, scan, and count rate settings should be controlled to achieve best results. Absolute intensities also can be corrected by the change in intensity observed for each diffractometer during monthly standards checks. When analyzing a glycol-solvated powder of clays, place an open dish or moistened sponge/towel of glycol near the sample holder to maintain solvation during the run(s). For heated powders of expandable clays, it is a good idea to re-scan the 10Å peak at regular intervals during the full scan. This allows an assessment of the rate of rehydration.

Carefully remove the cover slide from the bulk powder sample holder and center the sample in the holder of the instrument so that the maximum area of the powder is centered in the beam. Scale factors on older diffractometers with chart recorders should be set so that the most intense XRD peak required for quantification is as near to, but less than full chart-scale reading as possible. This can be accomplished by manually back-scanning from peak to peak before the forward scan is begun. If it is necessary to analyze a sample after ethylene glycol solvation or heating, samples should be loaded in holders and analyzed promptly to avoid glycol loss or H_2O gain by the sample. Analyze with Scintag® (40KV, 30MA, 1°2Θ/min, .03 chopper, 4° to 34°2Θ); obtain peak areas by "deconvolution" program; calculate by standard ratios (Qtz1:Qtz2 = 0.183; Qtz1:K-feld or plag = 0.391; Qtz1:calcite = 0.21; Qtz1:dolomite = 0.23; Qtz1:pyrite = 0.45; Qtz1:KCl = 0.138; Qtz2:KCl = 0.754); Note at time of this writing we also were estimating clay content as = 2 X 020 peak area/2 X 020 peak area + corrected Σnonclay intensities)

E. Calculations

Results can be quantified as peak heights or peak areas. If peak areas can be measured accurately, the results will generally be superior. However, in many cases, peak heights give perfectly adequate results. As a rule, nonclay minerals tend to be less variable in crystallinity than clay minerals. This makes peak height data from nonclays more reliable than those from clays. We also have found (during Mary Holden's thesis work) that the b-axis 020 or 02 band of kaolinite is about half as intense as that of the 2:1 clays such as illite, I/S, vermiculite, and smectite. It is not known what the relative 020 peak intensities are for chlorites. Variation in 020 intensity between different clays suggests that it may be useful to correct the 020 intensity from random powders, especially when that peak is used to estimate the total clay mineral content. In most cases, the best approach to complete quantitative analysis is to add an internal standard, calculate the nonclay minerals based on that standard, and proportion the clay minerals

as the percent remaining, i.e., 100-%nonclays. In many sample sets, it also may be possible to adjust the intensity factor of illite, I/S, vermiculite, smectite, and chlorite after estimating their Fe content from standard curves derived from NEWMOD® model XRD traces. If kaolinite is common in the sample set, it may be useful to add 5, 10, and 15 % of kaolinite with a similar "crystallinity" to a few of the samples to confirm kaolinite percentages based on difference from nonclays and/or compare the calculated LOI based on XRD with an actual LOI (see method A EOR/DOE).

Method 2. <2μm Sedimented Slides for Clay Mineral Stratigraphy (H.D. Glass; see Hughes and Warren, 1989

A. Uses

This method is primarily for Quaternary stratigraphic and soil profile analysis, but may be employed on any samples that disperse in water. The results can be used as a preliminary indicator of whole-sample content, especially when particle size data are available. However, other methods should be used for whole-sample analysis and for total characterization of clay minerals.

B. Equipment

Hamilton Beach mixer and cup or equivalent, small beakers (suggest 100 ml), 27x46 mm glass petrographic slides, (25 mm round glass disks for Scintag), 2- 1/4" to 1/2" x 3' glass rods, approximately 12" diameter desiccator jar, ethylene glycol, sodium hexametaphosphate (Calgon), stirring rod, eyedropper, timer, and furnace capable of 550°C.

C. Sample Preparation

1. For argillaceous samples (tills, loesses, and lacustrine samples), fill ~half of a 100 ml beaker with dry material. If the material contains little clay, more sample should be used. If the material is cemented with carbonates or contains large amounts of organic matter, it may be necessary to remove the carbonates with dilute (20%) acetic acid and/or the organic matter with NaOCl. Fill the 100 ml beaker with demineralized water. Let samples soak until slaked or overnight.

2. Stir and pour contents of 100 ml beaker into Hamilton Beech mixer cup; add another 100 ml of demineralized water; mix for 1 minute with the mixer on high; after a few seconds settling, fill the original 100 ml beaker and discard the remainder. If little clay is present, repeatedly add water, stir, and pour off fines into one or more beakers; allow samples to flocculate and settle overnight. The goal of these steps in the sample preparation is to obtain a flocculated layer of fine material equal to 1/4 - 3/8" in the bottom of the 100 ml beaker (or the proportional equivalent in other beaker sizes). This is an important goal; subsequent precision depends on consistent clay content. Normally

the sediment layer will be greater than 3/8", and the mixture will have to be diluted. This is done by estimating the dilution required to give 1/4 - 3/8" of sediment, pouring off the clear supernate, refilling with water, and stirring and discarding the proportion estimated to give 1/4 - 3/8" sediment. For example, if the overnight sediment layer is 1" thick, about 3/4 of the stirred material will have to be discarded. Next, refill with water, stir, and allow to flocculate. In cases of too little clay, the volume of water may be reduced to achieve proportionality of sediment:total volume. Continue to pour off clear supernate and refill until material is partially dispersed. If the material disperses after mixing, it may be desirable to add $CaCl_2$ to flocculate it, or the sample should be diluted to give about the slurry concentration of other samples in the set. In cases where a dispersed fine material has been concentrated from a sandy material, it is essential to flocculate the sample and concentrate the fines.

3. Sedimented slides are prepared by labeling a clean glass slide for each sample; placing the slides on two parallel glass rods spaced about half slide length apart on a level bench (these rods serve to raise the slides above the bench, so that a spill will run off without damaging other nearby slides); adding a few grains of sodium hexametaphosphate (Calgon®) to each sample; stirring each sample for ~ 15 seconds; and beginning a 15-minute timing with the first sample. After the samples have settled 15 minutes, draw off ~ 1 ml in an eyedropper or pipette from the upper 0.5 cm of the suspension and spread it uniformly on a standard petrographic slide; continue drawing off and making slides at ~ 15 sec intervals through the set. (Note: the 15 sec interval places a sample limit of < 60 on the number of slides that can be made at one time.) If the suspension on the slide contains too little clay, it may be possible to add 2 ml or so at the start, and, if necessary, to carefully add another 1 ml or so to the corner of the slide after it has <u>partially</u> dried (the sample must still be wet but the thickness of the suspension will decrease as water evaporates). Allow the samples to dry and then place them in an ethylene glycol-saturated atmosphere (desiccator jar with a 0.5 - 1" pool of ethylene glycol on the bottom and preferably warmed to 28°C) for at least two days prior to XRD analysis.

D. XRD

Analyze by XRD immediately after removing from glycolator. Set scale factors so that all clay peaks are on scale. If it is necessary or desirable to run another XRD scan after heating the slide at 300-350°C for one hour, for example to determine an accurate background or the amount of expandables (E), set the scale factor for the trace of the glycolated sample so that 10Å peak is less than or equal to half-scale on linear scale machines--otherwise the heated illite (I) peaks will be off scale. (See method 4, below, for heating techniques). It also is useful to record a visual or measured slide color. When analyzing a glycol-solvated sample, place an open dish or moistened sponge/towel of glycol near the sample holder to maintain solvation during the run(s). In order to assess the rate of rehydration of heated slides, it is a good idea to re-scan the 10Å peak at regular intervals during the full scan.

E. Calculations

Carry out the calculations by measuring appropriate peak heights or areas, using factors for log or linear scale, recording nonclay peak intensities, and calculating all indices required in the sample set as shown in Method I in Reference V.

Note that these analyses are mainly for stratigraphic purposes. Other methods should be used to estimate material properties or attempt bulk material balances. It is important to be sure that all measures of mineral content support stratigraphic picks. For example, two tills should have comparable E, I, kaolinite + chlorite (K+C), and carbonate contents if they are equivalent. Weathering generally increases the apparent illite content, and it may increase expandables. Great care must be taken to compare altered and unaltered materials or to adjust for weathering-- for example see T. C. I. (Hughes and Warren, 1989) for parent materials that lack significant chlorite.

Method 3. Whole-Sample or Size-Fraction Smear

A. Uses

For bulk-sample estimates of clay mineral content, for material characterization, and mass balance studies, such as source sediment - weathering - diagenesis investigations. Size-fraction smears also can be used to reduce turn around time and to eliminate errors caused by the effects of differential settling rates of various clay minerals on sedimented slides. (See Method III in Hughes and Warren, 1989).

CAUTION: CRYSTALLINE SILICA IS A PROBABLE RESPIRATORY *CARCINOGEN*, AND YOU SHOULD HANDLE ALL MINERAL POWDERS IN A FUME HOOD AND SOMETIMES WHILE WEARING A RESPIRATOR IS SOMETIMES REQUIRED.

B. Equipment required

A medium-sized mortar ($\sim$100 mm) and pestle, a micronizer, or the McCrone® mill; a double-bladed microspatula; desiccator jar filled with ethylene glycol as in Method 2; assorted beakers for size-fraction smears or sedimented slides; centrifuge, centrifuge tubes, and bottles; $CaCl_2$ and dilute (10%) HCl for flocculants; solution "A" of 200 g/l Calgon and 50 g/l Na_2CO_3 and solution "B" of 4-5 drops of solution A in 15 ml distilled water in an eyedropper bottle; 27x46 mm glass slides; 25 mm round glass disks (for Scintag); stiff artist's brush; furnace capable of heating to 550°C.

C. Sample preparation

1. For bulk samples, the dried sample is pulverized or lightly ground so that a few ml of the material will be representative. **In fume hood**, place about half of the end of a

microspatula (a few ml) of sample in a medium (~ 100 mm diameter) mortar and thoroughly grind until the material is smeared on the mortar; brush the powder onto a labeled petrographic slide; add dilute dispersant/buffer solution B drop-wise to powder while mixing with microspatula until a thin paste is formed; smear by spreading the paste uniformly over the slide with the microspatula sub-parallel to the slide; practice may be required to obtain a thin, even coating on the slide (Note that we have discovered that it is helpful to hold the slide by attaching a vacuum hose to the slide back for smearing); allow slide to dry and proceed to solvate with ethylene glycol, analyze with XRD, heat at 300-350°C and analyze with XRD as in Method 4 below. For preparation with a McCrone® mill, follow procedures above under Method 1 and use water as the grinding medium, unless a standard or unknown phase is water soluble; after centrifugation, pour off clear supernate, thoroughly mix sediment in bottom of tube, and, using a microspatula, smear a thin, even layer of the paste on a labelled glass disk or slide.

2. For size fractions – During the 1970s, samples were prepared by intensive grinding in a Waring blender, dispersion similar to Method 2 above, separation of a <2μm fraction (one pour off), flocculation and centrifugation to concentrate the clay fraction as a thin paste, and smearing pastes on petrographic slides. Most of the analyses for the Clay Section in the 1970s were made with this method and the calculation method given for Method II in (Hughes and Warren, 1989).

Virtually any size fraction can be smeared in this way. If high precision is required, the size classification step should be repeated 3 or 4 times to remove all of the required fraction. Fractions with particles coarser than ~10μm may require additional grinding before the smear slide is prepared. [The best particle size interval for making size-interval cuts is $\sqrt{2}$d (i.e., where d is the particle diameter and the size cuts are <0.25, 0.25-0.37, 0.37-0.5, etc.) although d/2 is perfectly adequate for most purposes--i.e., <0.25μm, 0.25-0.5μm, 0.5-1μm, etc.] Settling and centrifugation times are on file in the Unit office and are posted near the centrifuge in the wet lab (room 338).

D. XRD Analysis

Instrument scale factors should be set as in Method 2. A scan of the ethylene glycol-solvated and 300-350°C-heated sample is required for calculations. It may be useful in some cases to run the air-dried sample. In special cases where hydrated clay minerals such as halloysite may be present, it is usually helpful to scan a wet smear of the bulk sample, or a size fraction of the sample, before it dries. When analyzing a glycol-solvated sample, place an open dish or moistened sponge/towel of glycol near the sample holder to maintain solvation during the run(s). In order to assess the rate of rehydration of heated slides, it is a good idea to re-scan the 10Å peak at regular intervals during the full scan.

E. Calculations

Use the method described under Method III, in Hughes and Warren, 1989. Some care should be taken to distinguish between uncorrected and corrected %I and %E. Furthermore, because the degree of preferred orientation of clay particles increases with increasing clay mineral content, the clay index is not a percentage.

Method 4. <2μm Sedimented Slides

A. Uses

This method is often used in conjunction with Method 3 to provide a better qualitative analysis of the clay mineral fraction. It also can be used for rapid analysis of materials in the same manner as for Method 2. The same cautions mentioned for Methods 2 and 3 are appropriate here.

B. Equipment required

The same equipment is required here as for Method 2 above; however, mixing 30 sec to 1 min with an ultrasonic probe is generally substituted for the Hamilton-Beach mixer step.

C. Sample Preparation

1. Follow the same steps as in Method 2, except for substitution of ultrasonic mixing. Other mixers may be substituted, and easily dispersible materials may be processed without mixing. The ratio of flocculated sediment:total volume ratio should be about the same as in Method 2.

2. When the suspension is partially dispersed, add 2 drops of solution A. Adopt a consistent time of settling between 15 and 30 min (48 min are required for a 2.0 μm particle to settle 1 cm). REH uses 20 minutes settling and places ~ 2 ml of the top of the suspension on a standard petrographic slide or ~0.7 ml of the top of the suspension on a glass or metal disk for the Scintag. Dry slides on glass rods as in Method 2.

D. XRD Analysis

Set factors and scan slides as recommended for the other methods. It may be useful to run and XRD trace of slides after air-drying and ~450°C to detect certain forms of K/E, and some samples may require heating to 550°C to confirm loss of kaolinite or presence of chlorite. When analyzing a glycol-solvated sample, place an open dish or moistened sponge/towel of glycol near the sample holder to maintain solvation during the run(s). In order to assess the rate of rehydration of the expandables on heated slides, it is a good idea to re-scan the 10Å peak at regular intervals during the full scan.

E. Calculations

Use method III in Hughes and Warren, 1989. For Quaternary materials Method I in the same reference also may be used with these data.

Summary

These methods are based on the best approximation of the diffraction effects from "standard" minerals available at the ISGS over the past several decades. Different methods are typically designed for a specific purpose(s), and most will work best if applied to materials that are similar to those for which the method was developed. Although results can be surprisingly accurate, great care should be taken in the interpretation of results. It is important to remember that the apparent kaolinite content of a sample can vary by an order of magnitude due to the crystallinity of the kaolinite. The relative diffraction effect for chlorite in different samples is largely unknown. We have reported results as parts-in-ten or as percentages. Reports of tenths or hundredths of percent are inappropriate, except when averaging the results of a large number of samples or where a low-percentage clay fraction is normalized to a whole-sample basis in materials such as coals, sandstones, or limestones. In the latter case, the clay fraction is normally reported on a 100% basis and then normalized in tenths of percent on a whole-sample basis.

A recent improvement for XRD of clay minerals allows one to use NEWMOD® to calculate reference intensity ratios (RIRs). This eliminates the need for pure reference standards, and it makes possible the adjustments for crystallite size and other factors that can be adjusted with this program. Although we currently lack Dean Smith's computer program for calculating XRD patterns of nonclay minerals, this program can be used in the same way to obtain RIRs of nonclays.

The most common error in mineralogical analyses of this type is to present the appropriate cautions about accuracy in the methods section of a report and then construct elaborate explanations of small differences in clay mineral content in the results section of the same report.

It is a general misconception that the newest, and preferably computerized instrument, is the best for all types of problems. Each instrument in our laboratory has particular advantages and disadvantages, and it is by no means true that the older instruments are of less value in solving problems– in some cases the older units provide critical data that simply cannot be obtained on the computer-controlled Scintag® diffractometer.

The new standard for the ISGS for replicate analyses suggested by R. A. Griffin is a minimum of 10-15%. Actually, chemists typically use 5% blank analyses and 10% replicates. Although it is a good idea to run an XRD trace of the glass slides, cover slips,

disks, and sample holders to recognize "show through" when it occurs, blank analyses have little value in XRD. In cases where high precision and/or accuracy are required, it may be necessary to run more replicates. H. D. Glass has always run 100% replicates to catch preparation and calculation errors, and to detect changes in the instrument. Another value of replicate analyses is to eliminate analyst bias and measure analyst error. On some projects, it may be necessary to maintain "double blind" procedures from point of sampling to report preparation.

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Project Plan and Review - QA/QC

Project Title: DOE/EOR--Clays **ISGS Program:** Oil & Gas **Project Leader:** R. Hughes
Other Investigators: D. Moore, D. S. Beaty, J. P. Fagan, H. Glass

Objectives/Purposes: Project is designed to provide accurate and precise mineralogical analyses for the task force effort headed by D. F. Oltz. Secondary objectives are to examine the mineralogical results for correlations that might be of use **to the overall** project or to oil producers in the State, to estimate the likelihood of production problems from minerals found in each reservoir, and to extend our knowledge of the occurrence of minerals in reservoirs and their response to various strategies for increased production.

Project tasks and planned start/end dates: As determined by the U. S. DOE and ENR (ISGS) and by D. F. Oltz.

Procedures for Data Compilation - As given in attached SOP-QA/QC forms.

Facilities - Work is carried out in Rooms 316, 321, and 338 of the Natural Resources Building, Illinois State Geological Survey (Industrial Minerals Section, Clay Minerals Unit).

Data Records

		File storage locations		
Task #	Record (brief title)	Disk & Hard copy	Directory	Computer
All analytical data	EOR (Rm 316)		EOR/field	SE30(319)

Initial publication plan:

Publications on chlorite, clay mineralogy, and acid reactivity of clays are planned.

Planned schedule of project reviews: Reviews held at the request of D. Oltz and DOE. Scheduled QA/QC reviews about every 6 months--November and May.

Reports: DOE reports are required 2 per year. Also report all Board Reports, and, as each field is completed, to D. Oltz.

Changes: Began using 7.0% KCI std adds in July, 1991. Also began using KCI sat propanol and micronizer cup wash in August 1991.